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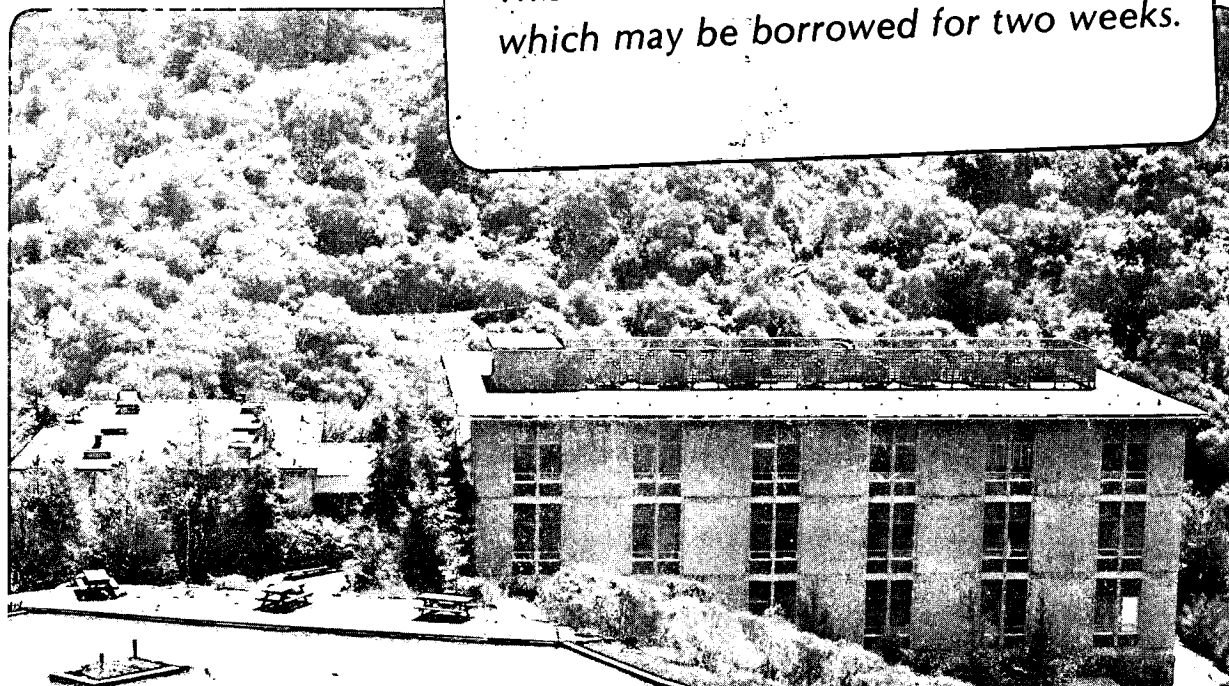
Final Report

H. Heinemann, G.A. Somorjai, and J.G. de la Banda

February 1989

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Final Report of Project 8594

"IMPROVED INDUSTRIAL CATALYSTS"

Part 1

Catalysts for NO and NO_x Removal

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FINAL REPORT

SUMMARY

The proposal on which this work was based was to study surface characteristics of different catalysts for the abatement of NO_x pollution and for hydrodesulfurization and hydrodenitrification in order to understand phenomena and mechanisms of the reactions and on this basis prepare better catalysts. During the course of the work, funding was abbreviated and the studies on HDS and HDN reactions had to be terminated. In the work on NO_x removal it was found early on that if one wanted to use pelleted catalysts rather than honeycomb catalysts, methods had to be found to increase the hardness of the pellets so they would withstand the abrasion that might occur at the high space velocities required. It was found that extrusion of vanadia-titania catalysts in the presence of phosphoric acid could give catalysts of sufficient hardness. However, catalytic activity of these catalysts was diminished because of formation of vanadium and of titanium phosphates. The presence of these phosphates was established by both ESR and XPS data. The decline in initial activity of the phosphoric acid extruded catalysts was of the order of about 10% and this may well be acceptable in view of the greatly improved hardness. Commercial catalysts currently in use consist of vanadia-titania extruded in honeycomb form to catalyze the reaction of NO_x with ammonia. Producing these honeycombs is a difficult and very expensive step. Pellets of the type described in this report are inexpensive to make and the small decline in activity they exhibit could be completely corrected by using a somewhat larger quantity of them, in other words, decreasing the space velocity. Life tests of these catalysts indicated that the initial activity decline did not interfere with long term stability of the catalyst, which performed at a somewhat lower level than the phosphorus free catalyst.

Extensive studies of the mechanisms involved in the reaction between NO_x and NH_3 by various surface science techniques, by ERS, and by XRD permitted conclusions to indicate that the reaction is based on a redox type mechanism. Ammonia reduces 5 valent vanadium species to vanadyl species and is in turn oxidized. Vanadia does not adsorb NO_x . Titania sorbs NO_x and the vanadyl species formed by a reduction with ammonia are eventually oxidized back to 5 valent vanadium by NO_x , which it is hypothesized spills over from titania sites to the vanadium sites. It is also clear that vanadyl species can form complexes with ammonia which, of course, deny access to NO species unless the complex is destroyed. The role of oxygen appears to be to destroy the adsorbed complexes. It is clear from this mechanism that two factors are of major importance in producing better catalysts: 1) Maximum dispersion of vanadia on titania to provide the largest possible number of vanadia sites on the external surface of the titania since the reaction is at too high space velocities for any diffusion to occur. 2) Titania to have the maximum ability to sorb NO_x , which probably means to have the highest surface area possible. Future work will have to follow the leads thus uncovered.

I. SELECTIVE CATALYTIC REDUCTION OF NO_x

A. FACILITIES IN MADRID

A.1. EQUIPMENT AND PROCEDURES FOR CATALYST PREPARATION

Method of Preparation

The catalysts used in this study were prepared on a titanium dioxide support and contain different amounts of the oxides of vanadium and tungsten. To prepare these catalysts we started with a solution of ammonium vanadate and ammonium tungstate [NH_4VO_3 (Merck) and $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{14} \cdot 5\text{H}_2\text{O}$ (Prolabo)] which was added to a titanium hydroxide paste, CLDD 1727 (Tioxide). The resulting paste is concentrated by drying to a powder. The resulting mixture was ground and sieved to a powder which was ready for extrusion and which will be termed "powder precursor" in this report (P).

For the preparation of the extrudate, the previously described powder is mixed with a solution of phosphoric acid and is homogenized and extruded and dried at room temperature obtaining an extrudate which in this report is named "fresh extrudate"(F).

The extrudate is dried in an oven at 110°C during 12 hours and following this is treated in a tubular reactor at 500°C during 4 hours, in an air flow of 60 ml/min; the resulting product is designated "treated catalyst"(T).

The commercial vanadia-titania-tungsten oxide catalyst (CC) was obtained from a manufacturer for comparative purposes.

Equipment was available for BET surface area and void volume determinations, for mercury porosimetry, infra red studies, TDS, XRD, ESR, and XPS. Chemical analysis was carried out by conventional means, such as x-ray fluorescence.

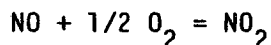
Catalyst Testing

Catalytic activity was measured in a tubular integral reactor. The operating conditions were established to reproduce the composition of

the acid gases of a nitric acid plant:

$$\begin{aligned}\text{NO}_x &= 3000 \text{ Vpm} \\ \text{O}_2 &= 3.0\% \text{ vol} \\ \text{N}_2 &= \text{balance}\end{aligned}$$

The molar ratio of $\text{NO}_2:\text{NO}$ was maintained at close to unity. Since it was necessary in order to obtain the NO_x composition from a mixture of NO (10%) in nitrogen, it was necessary to provide a special system of burettes in the feed system in order to convert part of the NO to NO_2 in homogeneous phase according to the reaction:



In order to obtain the desired $\text{NO}_2:\text{NO}$ ratio at the entrance of the reactor, it is necessary to control the concentration of NO and oxygen as well as the temperature and time of contact between the gases. Ammonia was fed directly to the entrance of the catalytic reactor in order to avoid formation of salts of ammonia. The analysis of the $\text{NO}:\text{NO}_2$ concentration at the entrance of the reactor was carried out with chemiluminescence using a luminol analyzer "LUMINOX (B.O.C.)." The analysis of ammonia and of N_2O was carried out by infrared spectroscopy using a Miran 1.A (Foxboro) spectrometer.

Crushing Strength (Hardness)

The hardness was measured using a Chatillon dynamometer, Model DPP. The magnitude measured has been the force that can be applied between two parallel planes limiting the pellet before the pellet breaks down.

This measure has been considered in this study only in order to compare different catalysts and see the influence of the different variables on hardness. Nevertheless, measurements with commercial catalysts allowed us to consider as an acceptable value for commercial uses, in horizontal position, with a cylinder length of 5 mm, the value of 5 K_p .

Figure 1 shows a general scheme of the experimental system.

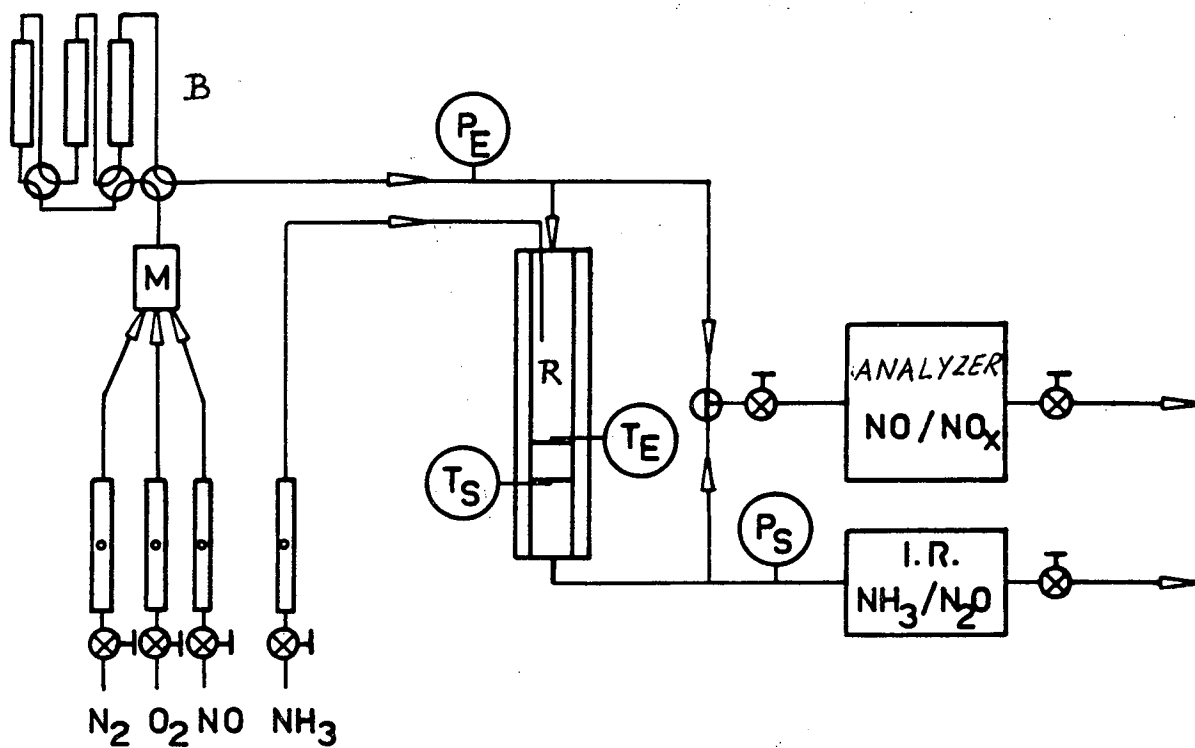


Fig. 1

- (M) Mixer
- (B) Burettes for production of NO_2 from NO
- (R) Reactor
- (AIL) Dilution System
- (P_E , P_S) Manometers
- (T_E , T_S) Thermocouples

Hardness

I.

B) FACILITIES IN BERKELEY

X-ray photon spectroscopy and Auger electron spectroscopy were carried out in equipment described in various publications [*] and which is also shown in Fig. 31 of this report. Life tests of catalysts were obtained in a fully automated unit which permitted control of gas flows, pressure and temperature, recording all data. The unit operated on a 24 hour/day, 7 day/week basis. Gases exiting the unit were analyzed in Berkeley by the procedure previously described in the section on "Facilities in Madrid."

*Blakely, D.W., Kozak, E.I., Sexton, B.A., and Somorjai, G.A., J. Vac. Sci. Technol., 13, 1091 (1976)

C) RESULTS

Work performed in Berkeley will be described in this report in the sections C.7 "Catalyst Life," section C.8 "Adsorption and Spectroscopic Measurements and Mechanistic Considerations," and section C.1 "Catalyst Preparation."

C.1 CATALYST PREPARATION

Nomenclature

The catalysts used in this study have been designated with a number which identifies each batch prepared. The nomenclature explained below was used to identify catalysts prepared by different batches during the preparation process. First, there is a letter "P" or "E" which stands for "Powder" (without agglomerates) or for "Extrudates."

Further, there are three numbers separated by periods which correspond to the relative atomic ratios of titanium, vanadium, and tungsten which existed in the precursory powder of the catalyst. Following the numbers, there is an "S" or a "C." "S" refers to a paste which has been neutralized and washed and, therefore, has a low sulfate ion content. "C" corresponds to a starting paste with appreciable sulfate ion concentrations (approximately 8%) which has not been washed.

Following this there is a number which relates to the dilution of the H_3PO_4 in water which was used for the extrusion (0, 1, 3, or 5) or a letter "N" when HNO_3 was used for agglomeration or a (-) in the case in which the extrusion was only with water.

Finally, there is a letter "F" or "T." "F" stands for a sample which has not been heat treated and "T" for a sample which has been heat treated at 500°C.

Catalysts Prepared

The catalysts prepared have been classified in ten series depending on their composition.

Series "S" (without sulfate)

In the catalysts of this series, the precursory TiO_2 paste used ($\text{pH} = 1.5$, $\text{SO}_4^{2-} = 8\%$), was neutralized with an aqueous solution of ammonia and successively washed until there was no apparent precipitation of BaSO_4 when the wash water was treated with a saturated solution of Ba(OH)_2 .

In the catalysts of this series, relative atomic ratio of vanadium and tungsten was changed, but the total amount of vanadium and tungsten in the precursor powder was constant and equivalent to 10%. These catalysts were extruded with phosphoric acid in such a proportion that the phosphorous content of the product was about 14% by weight. The changes in phosphorous content which have been observed are due to the fact that the ease of extrusion is dependent on the relative ratio of vanadium and tungsten and that, therefore, the amount of powder required for good extrusion changes.

In Table 1 the global composition of the catalysts of this series is shown (after heat treatment at 500°C) and is expressed in wt.%.

TABLE 1.
Composition of Series "S" Catalysts

Cat. No	Nomenclature Ti:V:W	Composition (% weight)				
		Ti	V	W	P	S
E202	E90.10.0 S3T	34.1	4.0	-	15.3	0.7
E203	E90. 8.2 S3T	32.5	3.5	3.2	15.5	0.8
E204	E90. 5.5 S3T	30.2	2.0	6.8	13.9	0.7
E205	E90. 2.8 S3T	30.0	0.8	11.1	14.0	0.7
E224	E90.0.10 S3T	36.0	-	12.3	12.7	0.6

Series "C" (with sulfate)

The catalysts of this series were obtained in the same manner as those of Series "S" (atomic ratio Ti:V + W = 90:10), by utilizing the precursary TiO_2 paste without neutralization or washing, that is with a sulfur content of 8% by wt. The phosphorus content was maintained at about 14% by wt.

TABLE 2.
Composition of Series "C" Catalysts

Cat. No	Nomenclature Ti:V:W	Composition (% weight)				
		Ti	V	W	P	S
E201	E90.10.0 C3T	33.1	3.8	-	14.7	1.8
E218	E90. 8.2 C3T	32.4	3.1	2.8	15.1	1.7
E208	E90. 5.5 C3T	30.2	2.1	7.2	14.9	1.3
E209	E90. 2.8 C3T	30.0	0.8	10.9	13.3	1.4
E210	E90.0.10 C3T	28.0	-	12.6	12.2	1.1

Series "P" (with phosphorus)

In the catalysts of this series the major variable is the proportion of phosphorus in order to determine the effect of H_3PO_4 on the properties of the catalyst.

For the preparation, the precursor powder had an atomic ratio of $Ti:V:W = 90:8:2$, and the paste used was neutralized and washed (without sulfate) and the proportion of H_3PO_4 employed was varied.

The results obtained are presented in Table 3.

TABLE 3.
Composition of Series "P" Catalysts

Cat. No	Nomenclature $Ti:V:W$	Composition (% weight)				
		Ti	V	W	P	S
E214	E90. 8.2 S-T	41.6	4.6	4.0	-	0.9
E103	E90. 8.2 S5T	36.3	3.4	3.2	12.3	1.1
E111	E90. 8.2 S3T	32.5	3.2	3.0	14.7	1.2
E109	E90. 8.2 S1T	28.6	2.9	2.8	18.8	0.9
E110	E90. 8.2 S0T	24.2	2.8	2.6	22.3	0.8

Other series (W0, W5, and V5)

Another three series of catalysts were prepared using the original paste containing sulfate and containing a phosphorus content of about 14% by wt. In this series the atomic content of vanadium or tungsten was constant while the other component was varied. In this series the denomination: "W0", "W5" and "V5" is represented in Table 4 showing the

relative proportions of titanium, vanadium, and tungsten, keeping one of them constant.

TABLE 4.
Composition of V5, W0, and W5 Catalysts

Series	Cat. No	Nomenclature Ti÷V÷W	Composition (% weight)				
			Ti	V	W	P	S
V5	E233	E95. 5.0 C3T	37.0	2.0	-	14.5	1.7
	E227	E94. 5.1 C3T	35.0	2.0	1.4	15.7	1.6
	E226	E93. 5.2 C3T	33.2	2.4	3.3	15.5	1.4
	E220	E90. 5.5 C3T	30.2	2.1	7.2	14.9	1.3
	E228	E87. 5.8 C3T	30.8	1.9	10.5	13.6	1.2
W0	E233	E95. 5.0 C3T	37.0	2.0	-	14.5	1.9
	E201	E90.10.0 C3T	33.1	3.8	-	14.7	1.8
	E234	E80.20.0 C3T	24.4	8.2	-	19.5	1.0
W5	E230	E94. 1.5 C3T	30.2	0.6	8.3	16.5	1.6
	E229	E93. 2.5 C3T	32.8	0.9	8.2	13.0	1.5
	E208	E90. 5.5 C3T	30.2	2.1	7.2	14.9	1.3
	E231	E87. 8.5 C3T	29.6	2.8	6.7	15.0	1.3

Series "P" "

The catalysts in this series were prepared from the same precursor powder by varying the concentration of phosphoric acid used in the extrusion step. The atomic ratio of Ti÷V÷W was 87÷5÷8 and the characteristics of these materials are shown in Table 5.

TABLE 5.
Composition of Series "P" Catalysts

Cat. No	Nomenclature Ti÷V÷W	*Composition (% weight)			P	S
		Ti	V	W		
E242	87. 5.8. S-T	44.2	2.7	15.0	0	1.0
E243	87. 5.8. S32T	41.6	2.5	15.1	3.0	1.0
E246	87. 5.8. S7.5T	35.1	2.4	11.9	9.1	0.8

Series "T"

The catalysts in this series all have the same composition except they are heat treated at different temperatures, namely at 500, 600, 700, and 800°C respectively. Composition of these catalysts is shown in Table 6.

TABLE 6.
Composition of Series "T" Catalysts

Cat. No	Nomenclature Ti÷V÷W	*Composition (% weight)			P	S
		Ti	V	W		
E283	E90. 8.2 C5T500	35.3	3.3	2.9	11.4	1.1
E285	E90. 8.2 C5T600	35.3	3.3	2.9	11.4	1.1
E287	E90. 8.2 C5T700	35.3	3.3	2.9	11.4	0.7
E312	E90. 8.2 C5T800	35.3	3.3	2.9	11.4	0.4

*The percentage of S is obtained by x-ray fluorescence.

Series "C5"

The catalysts of this series were obtained in an analogous manner as those of series C3, but employing a more dilute solution of H_3PO_4 (F=5) and treating the catalysts at 700°C or 500°C respectively. Tables 7 and 8 show the composition of this series of catalysts.

TABLE 7.
Composition of Series C5T700 Catalysts

Cat. No	Nomenclature Ti:V:W	*Composition (% weight)				
		Ti	V	W	P	S
E276	E90.10.0 C5T700	35.3	4.2	0	11.5	0.7
E287	E90. 8.2 C5T700	36.9	3.5	2.4	11.3	0.7
E274	E90. 5.5 C5T700	34.7	2.2	7.6	10.5	0.6
E286	E90. 2.8 C5T700	32.6	0.8	11.7	10.8	0.7

*(The same as in Table 6)

TABLE 8.
Composition of Series C5T500 Catalysts

Cat. No	Nomenclature Ti:V:W	*Composition (% weight)				
		Ti	V	W	P	S
E275	E90.10.0 C5T500	35.3	4.2	0	12.2	2.0
E283	E90. 8.2 C5T500	31.1	3.4	2.9	11.5	1.1
E272	E90. 5.5 C5T500	34.7	2.2	7.6	10.5	1.5
E282	E90. 2.8 C5T500	32.6	0.8	11.7	10.8	1.4

*(The same as in Table 6)

Catalysts E-341 and E-352 (with Na)

Two catalysts (E-341 and E-352) were prepared which have the same relative composition in $Ti \div V \div W$ and P as the catalysts demoninated E-90-10-0 C₃T. Catalyst E-341 was made following the standard method with properties which are the same as those of catalyst E-201. For this preparation the starting material was the hydrated TiO_2 paste having a pH of 1.5.

For catalyst E-352 the same paste was neutralized with a solution of NaOH and the preparation continued identical with that of the other catalyst. The sodium content in catalyst E-352 is of the order of 2%. Composition of these catalysts is given in Table 9.

TABLE 9.
Composition of Catalysts E341 and E 352

Cat. No	Nomenclature $Ti \div V \div W$	Composition (% weight)					
		Ti	V	W	P	S	Na
E341	90.10.0 CST500	35.3	4.2	0	12.2	1.3	0
E352	90.10.0 CST500	33.9	4.0	0	11.8	1.2	2.0

C-2 CATALYST CHARACTERIZATION

In the following tables surface area in m^2/g is presented as is the apparent density and the catalyst crushing strengths. (The minimum acceptable hardness value is $5K_p$.)

Series "S"

TABLE 10.
Physical Characteristics of Series "S" Catalysts
(without sulfate)

Cat. #	Surface Area $\text{m}^2 \text{g}^{-1}$	App. Density g cm^{-3}	Hardness K_p
E-202	7.5	0.75	7.6
E-203	5.5	0.75	8.3
E-204	4.9	0.81	13.2
E-205	3.9	0.82	14.6
E-224	4.0	0.82	12.8

Series "C"

TABLE 11.
Physical Characteristics of Series "C" Catalysts
(with sulfate)

Cat. #	Surface Area $\text{m}^2 \text{g}^{-1}$	App. Density g cm^{-3}	Hardness K_p
E-201	8.2	0.76	8
E-218	6.0	0.83	9
E-208	5.0	0.80	12.6
E-209	4.3	0.81	15.8
E-210	4.0	0.87	13.8

Series "P"

TABLE 12.
Physical Characteristics of Series "P" Catalysts
(with variable phosphorus content)

Cat. #	Surface Area $\text{m}^2 \text{g}^{-1}$	App. Density g cm^{-3}	Hardness K_p
E-214	64.0	0.60	-
E-103	12.3	0.67	4.0
E-111	7.7	0.72	8.3
E-109	3.1	0.90	16.8
E-110	1.0	1.11	24.0

Other series (V5, W0, and W5)

TABLE 13.
Physical Characteristics of Series V5, W0, and W5 Catalysts

Series	Cat. #	Surface Area $\text{m}^2 \text{g}^{-1}$	App. Density g cm^{-3}	Hardness K_p
V-5	E-233	8.1	0.77	4.6
	E-227	6.6	0.76	8.9
	E-226	6.8	0.73	11.1
	E-220	6.0	0.80	14.4
	E-228	3.9	0.82	19.9
W-0	E-223	8.1	0.77	4.6
	E-201	8.2	0.76	4.4
	E-234	7.4	0.64	4.5
W-5	E-230	7.3	0.79	10.0
	E-229	4.7	0.71	11.5
	E-208	5.0	0.81	12.6
	E-231	4.8	0.83	17.9

Series P'

TABLE 14.
Physical Characteristics of Series P' Catalysts

Cat. #	Surface Area $\text{m}^2 \text{g}^{-1}$	App. Density g cm^{-3}	Hardness K_p
E-242	68.1	0.61	0
E-243	42.1	0.58	0
E-246	11.4	0.74	3.2

Series T

TABLE 15.
Physical Characteristics of Series "T" Catalysts
(with sulfate)

Cat. #	Surface Area $\text{m}^2 \text{g}^{-1}$	App. Density g cm^{-3}	Hardness K_p
E-283	8.5	0.8	5.1
E-285	9.6	0.8	6.3
E-287	8.3	0.7	5.1
E-312	0.4	0.8	4.5

Series C5

TABLE 16.
Physical Characteristics of Series C5T700 Catalysts

Cat. #	Surface Area $\text{m}^2 \text{g}^{-1}$	App. Density g cm^{-3}	Hardness K_p
E-276	9.5	0.72	5.4
E-287	8.3	0.74	5.1
E-274	10.8	0.82	9.2
E-286	7.4	0.89	7.8

TABLE 17.
Physical Characteristics of Series C5T500 Catalysts

Cat. #	Surface Area $\text{m}^2 \text{g}^{-1}$	App. Density g cm^{-3}	Hardness K_p
E-275	11.4	0.69	5.4
E-283	8.5	0.80	5.1
E-272	7.1	0.76	10.2
E-282	6.7		3.5

TABLE 18.
Physical Characteristics of Series C5T500 Catalysts

Cat. #	Surface Area $\text{m}^2 \text{g}^{-1}$	App. Density g cm^{-3}	Hardness K_p
E-314	11.4	1.25	5.4

C.3 EFFECTS OF VARIABLES

Effect of Phosphoric Acid

In a preliminary study made prior to this project, phosphoric acid in aqueous solution gave the best results as a binder.

In the catalysts of series "P" the amount of P was changed with the aim of studying its effect.

Figure 2 gives the values of surface area and hardness of the catalysts of series "P". It is clearly shown that when the P content increases there is a major increase in hardness. This increase in hardness parallels an increase in the apparent density of the solid (see Table 3) and a strong decrease in the surface area.

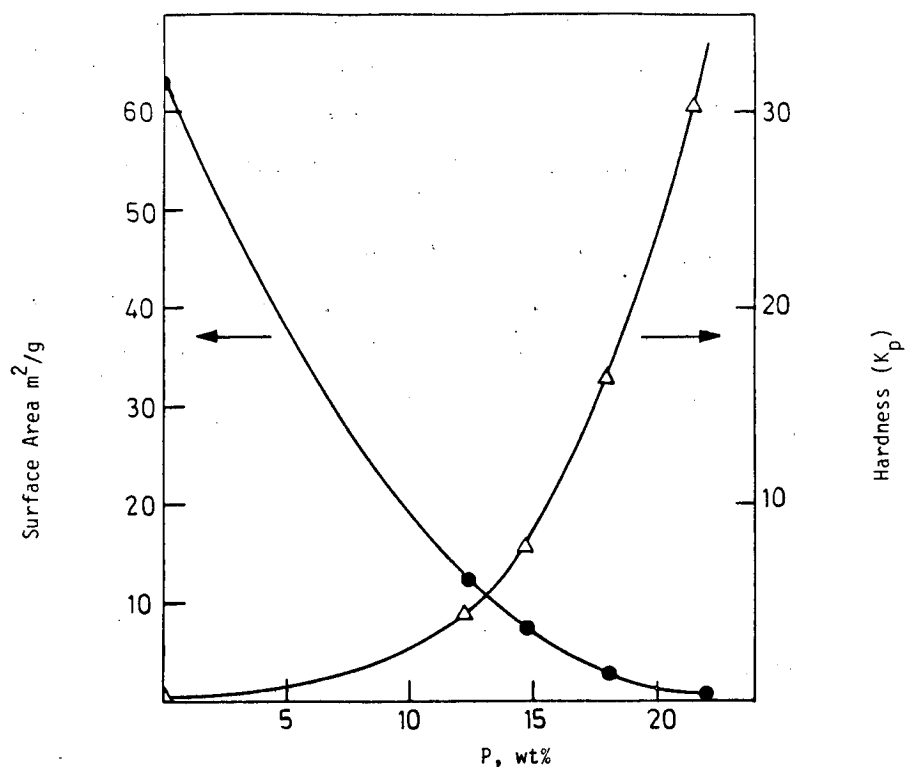


Fig. 2. Effect of phosphorus content of catalysts of series "P" on surface area and hardness.

Effect of Vanadium

Analyzing the results given in Table 4, for catalysts of series W0, it is observed that in the absence of tungsten the hardness is independent of the vanadium concentration. Neither the apparent density nor the surface area of the catalysts undergo major changes.

Nevertheless with catalysts containing tungsten (series W5) the increase in V content produces an increase in hardness. The surface area is clearly lower when the catalyst has tungsten than when it is tungsten free. On the other hand the vanadium percentage seems to have no effect on the surface area.

Effect of Tungsten

The data of Table 4, corresponding to catalysts of series V5, show a clear increase of hardness with W content.

It is important to point out that the hardness of these catalysts is also a function of the vanadium content, in such a way that comparing catalysts E 210 (90.0.10C3T) with catalyst E 228 (87.5.8C3T), it is observed that the latter is much harder, indicating that composition of the catalyst has a complex influence on hardness.

Figure 3 shows the change in hardness of series V5 catalysts as a function of W content. Also in this figure the change in specific surface for these catalysts has been plotted.

This figure also shows that when the tungsten content increases, the increase in hardness of the catalyst corresponds also to a decrease of its surface area.

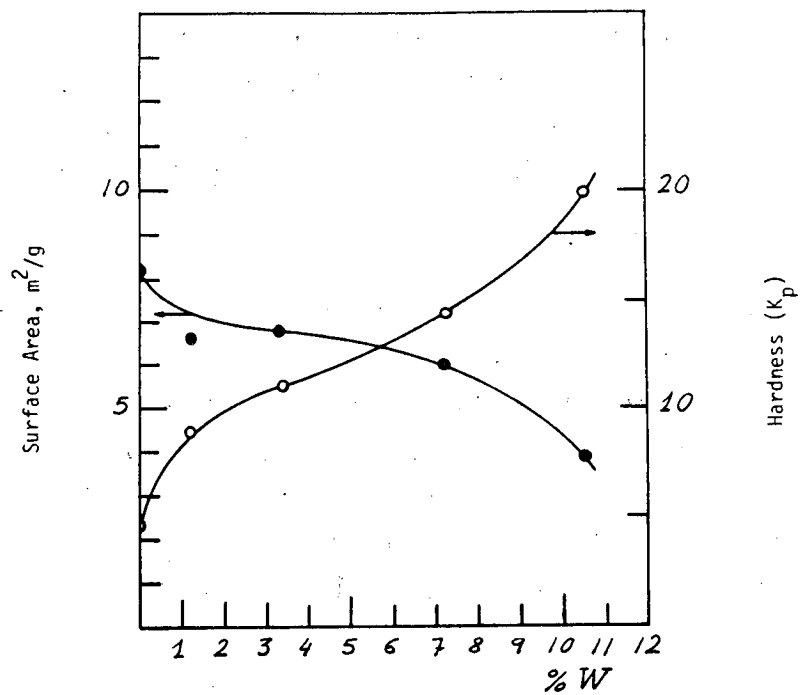


Fig. 3. Effect of tungsten content of catalysts of series "V5" on surface area and hardness.

Effect of the Atomic Ratio V:W and of the Sulfates

By comparing the results in Tables 1 and 2, which correspond to the properties of the catalysts of series "S" and "C", with changes of the ratio V:W, it can be shown that in each series, when the W proportion increases the specific surface decreases gradually and the hardness increases strongly in spite of the decrease of the phosphorus content.

These results are shown in Figures 4 and 5. Figure 4 shows that a maximum hardness is obtained when the atomic ratio of W is \geq than that of V. Nevertheless, when the ratio V:W decreases a progressive decline of the specific surface is noted (see Figure 5). From the results shown in Figure 5, it is also apparent that catalysts of series C (with sulphates) have a specific surface slightly higher than those belonging to series S (without sulphates) of equivalent composition.

C.4 EFFECT OF THE VARIABLES ON PHYSICAL PROPERTIES AND TEXTURE OF CATALYSTS

Effect of H_3PO_4

Results shown in Table 5 fully agree with those in Table 3E. This table shows that the increase of the P content in the catalyst produces an increase in the hardness and a decrease in specific surface (see Figure 6).

The analysis of the size and pore distribution of series P catalysts, by Hg porosimetry, shows that the decrease of total area is mainly due to a decrease of pores between 1000 and 2000 Å (Figure 7).

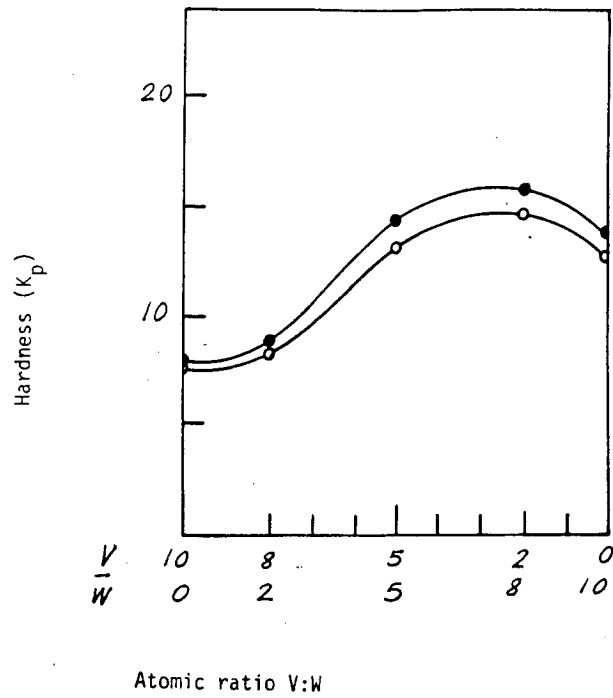


Fig. 4. Effect of the atomic ratio $V:W$ on hardness of catalysts of series "C" (with sulfate) (●) and "S" (without sulfate) (○) for the atomic ratio $Ti:(V+W)=90:10$.

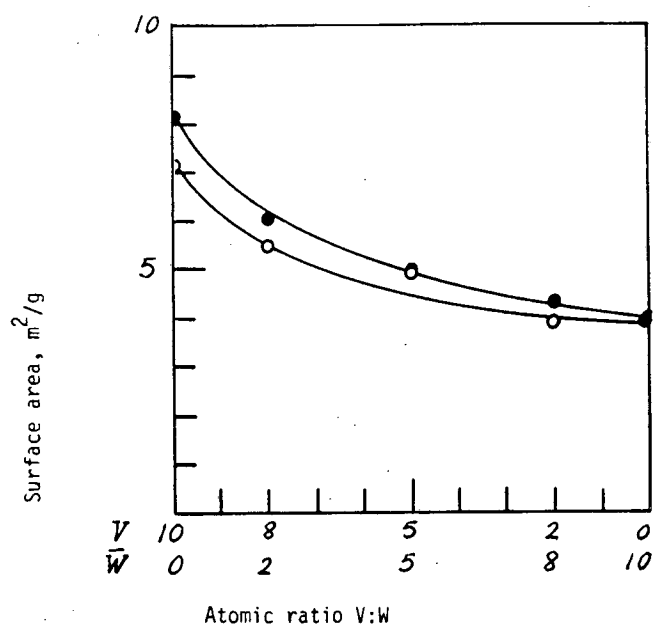


Fig. 5. Effect of atomic ratio $V:W$ on the surface area of catalysts of series "C" (with sulfate) (●) and "S" (without sulfate) (○) for the atomic ratio $\text{Ti}:(V+W)=90:10$.

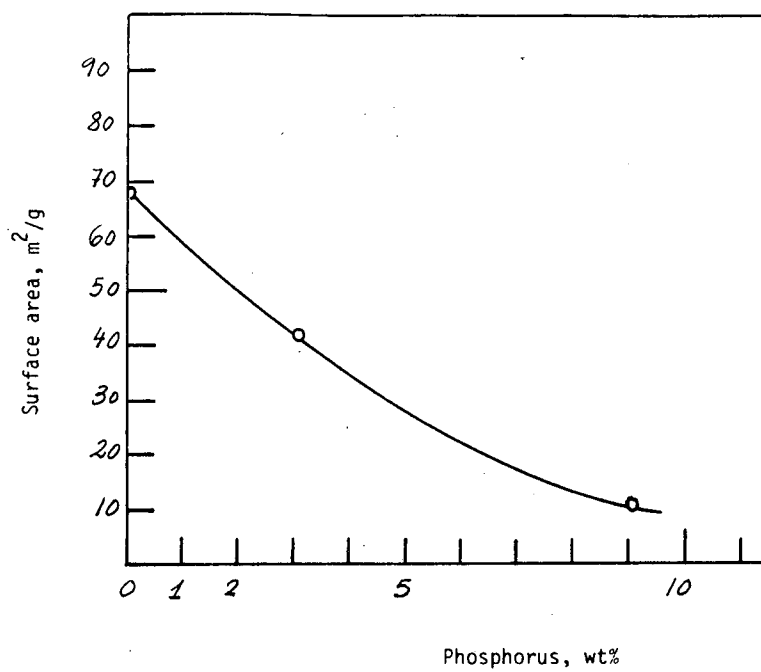


Fig. 6. Effect of P content on surface area.

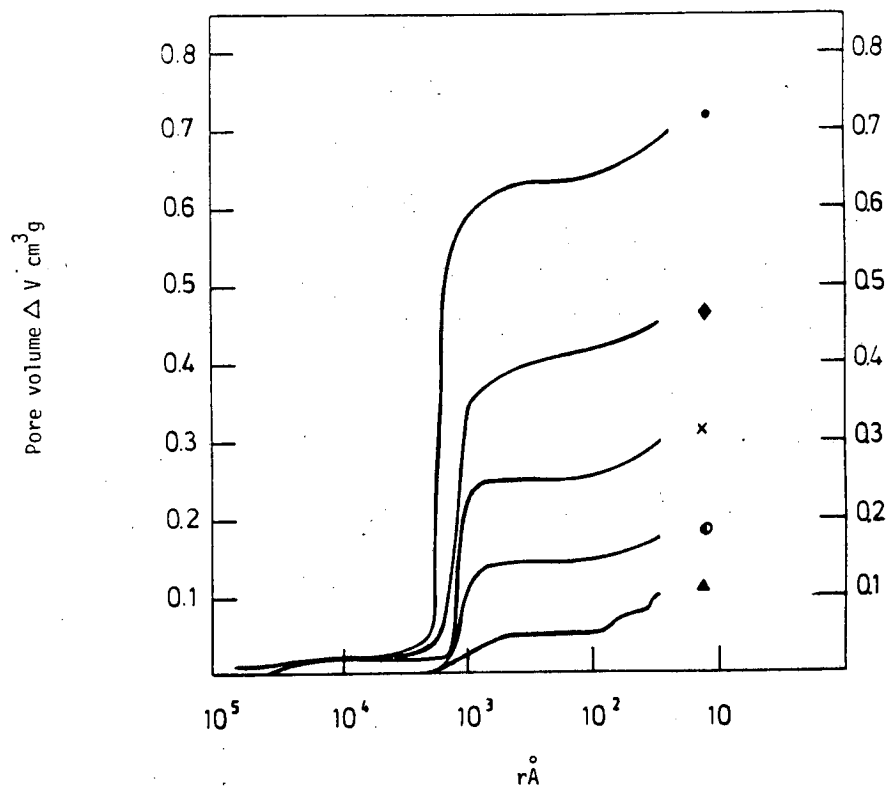


Fig. 7. Pore size distribution for series "P" catalysts. E-214 (●); E-103 (◆); E-111 (x); E-109 (◐); E-110 (▲)

Considering that operation with these catalysts is at very high space velocity, it is very likely that the contribution of these pores is very important and plays an important role in the process.

Effect of the Temperature of Pretreatment on the Catalysts

The catalysts of this series do not exhibit appreciable changes of physical properties; it seems though that there is a maximum in specific surface and strength when the catalyst is pretreated at 600°C.

The analysis of Hg porosimetry data shows that for these catalysts the contribution of pores of greater than 500 Å increases when pretreatment temperature increases.

Finally, thermogravimetric analysis shows that loss of sulphates mainly occurs between 450 and 600°C.

Effect of the Ratio W/V

Analysis of the results given in Tables 3 and 4 results in the same conclusions as those obtained from the results of series "S" and "C".

A maximum in the strength of the catalysts is obtained when the atomic ratio W/V is between 1 and 4.

C.5 CATALYST ACTIVITY (Nitric Acid Plants)

Determination of Operating Conditions

The catalyst used in these preliminary exploratory results was E 202 (E. 90.10.0 S3T).

During all the experiments, the total flow of feed gases ($F_T - 3.0 \text{ L N min}^{-1}$) and the space velocity (GHSV - 40.000 h^{-1}) were kept constant, that is, the volume of catalyst used in each run was 4.5 ml.

Effect of Reaction Temperature

Figure 8 shows the change of conversion both for each reactant (NO , NO_2 , and NH_3) and for global NO_x as a function of temperature.

Conversion has been defined as:

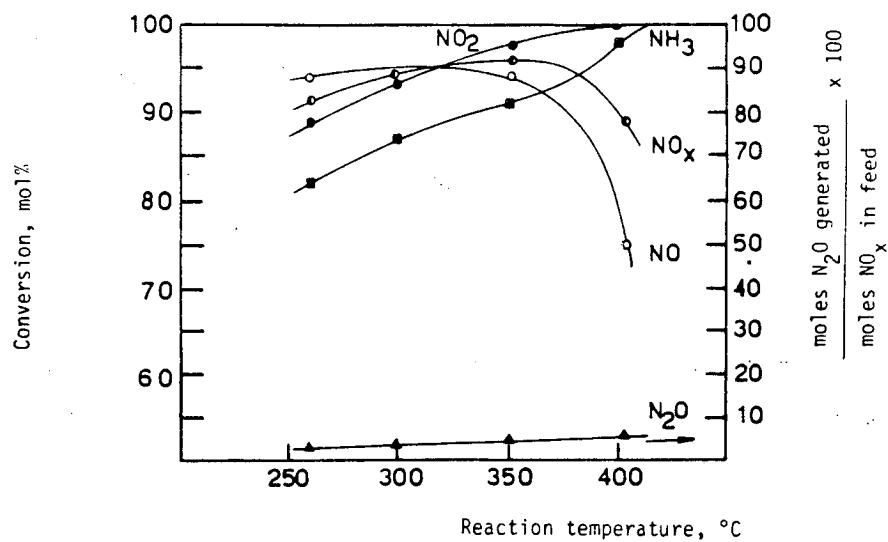
$$x_i = \frac{\text{moles } i \text{ (inlet)} - \text{moles } i \text{ (outlet)}}{\text{moles } i \text{ (inlet)}} \times 100$$

Also, in the lower part of the figure results of conversion to N_2O are shown. Due to the fact that in all the cases in which N_2O formed its concentration was either equal to or lower than 5% of the NH_3 in the feed, the presence of N_2O was not considered significant for kinetic effects.

In Figure 8 it is also shown that in the temperature range between 350 and 400°C , a considerable increase of NH_3 is observed with a simultaneous sharp drop of the NO conversion, causing a maximum in the curve of total conversion of NO_x at a reaction temperature between 350 and 450°C .

This decrease of NO conversion is due to an increase in the rate of oxidation of NH_3 by the O_2 present in the feed.

In order to know in detail the behavior of each catalyst with temperature, runs similar to those described in Figure 8 were performed for each catalyst, changing temperature between 250 and 350°C .



Operating conditions:

GHSV = 40.000 h^{-1}

Reactant concentrations: NO_x : 3000 vpm ($NO = 1400 \text{ vpm}$,
 $NO_2 = 1600 \text{ vpm}$)

NH_3 : 3300 vpm

O_2 : 3.0 %vol.

N_2 : balance

Catalyst: E202 (E.90.10.0S3T)

Fig. 8. Effect of reaction temperature on conversion of NO (○); NO_2 (●); NO_x (●); and on NH_3 (■) and NO_2 (▲) generated.

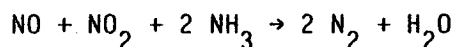
Two temperatures were considered as adequate for comparison of the activity of the catalysts:

- (a) 350°C, a temperature at which direct oxidation of NH_3 by O_2 is not observed.
- (b) 430°C, temperature at which both reactions compete.

Influence of NH_3 Concentration

From the point of view of industrial scale operation this is one of the more important parameters because, as can be seen in Figure 9, a lack of NH_3 in the feed causes a proportional decrease of conversion. Also an excess of NH_3 , (besides the useless expense involved) could lead to important safety problems, due to the possibility of formation of ammonia salts, with risk of explosion.

From this figure one can see that the reaction follows the stoichiometry:



Moreover, it is shown that when the ratio NH_3/NO_x is greater than 1, a very great increase of the NH_3 in the exit gas is produced. Considering these results, it was decided to perform the comparative tests for catalyst activity using a NH_3/NO_x ratio in the feed close to 1.

Effect of NO_2/NO Ratio and of the O_2 Concentration

These two parameters are closely linked, because either a higher or lower proportion of NO_2 in the sample of NO_x is obtained by changing the O_2 concentration in the gas phase.

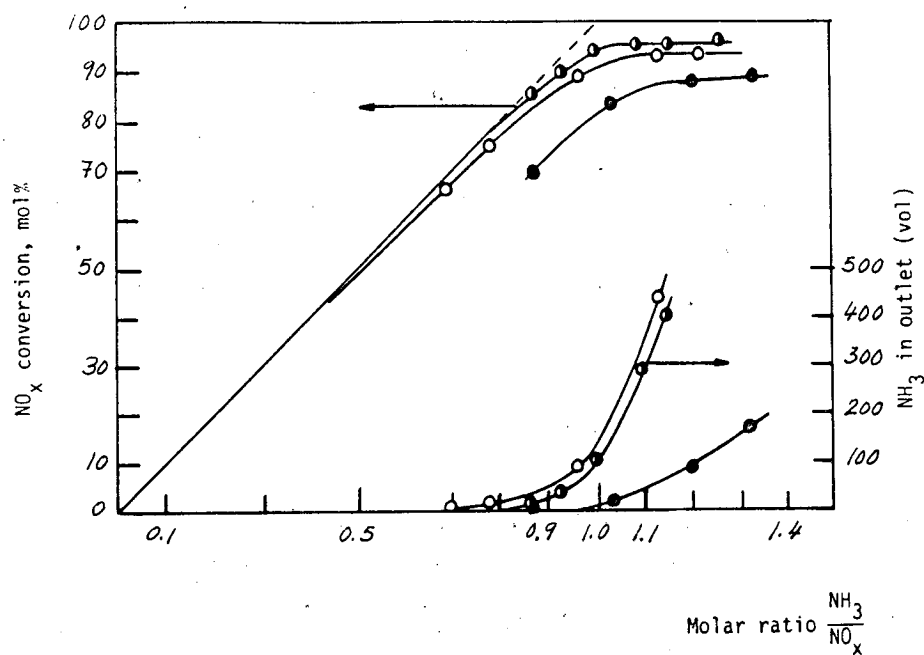


Fig. 9. Effect of $\text{NH}_3:\text{NO}_x$ in the feed on the global conversion of NO_x and on the NH_3 concentration at the reactor outlet.
 Temperatures: 300°C (○); 350°C (◐); 430°C (●)
 Catalyst E-202 (E.90.10.OS3T)

According to the results given in Figure 10, O_2 concentration is an important factor when only NO is in the feed, mainly at concentrations below 3%. Nevertheless, catalytic activity becomes independent of the O_2 content in the reactants at ratios $NO_2/NO > 0.5$ and $O_2 \geq 1\%$.

This fact allowed the control of the ratio NO_2/NO in a wide range by changing the concentration of O_2 . In Figure 11, the values of global conversion of NO_x obtained with this catalyst at 300° and $350^\circ C$ were plotted as a function of the ratio NO_2/NO in the feed. It is apparent that a maximum in activity is obtained when the ratio NO_2/NO is close to unity.

Operating Conditions

In consideration of the results obtained and of the characteristics of the exit gases of the nitric acid plants, it was decided to perform experiments with all the catalysts under the following conditions:

- Total gaseous flow: 3.0 L N min^{-1}
- Space velocity: $40,000 \text{ h}^{-1}$
- Gas composition:
 - NO_x : 3000 ppm (vol)
 - NH_3 : 3300 ppm (vol)
 - O_2 : 2-3%
 - N_2 : balance
- Molar ratio NO_2/NO : 1.0 - 1.1
- Reaction temperature: $250 - 450^\circ C$

Effect of Changes in Composition on the Catalysts

The effect of changing the content of phosphorus, vanadium, tungsten, and sulfates, and the atomic ration (V/W (keeping constant the amount V+W) on catalytic activity at the selected operating conditions has been studied. Results are as follows:

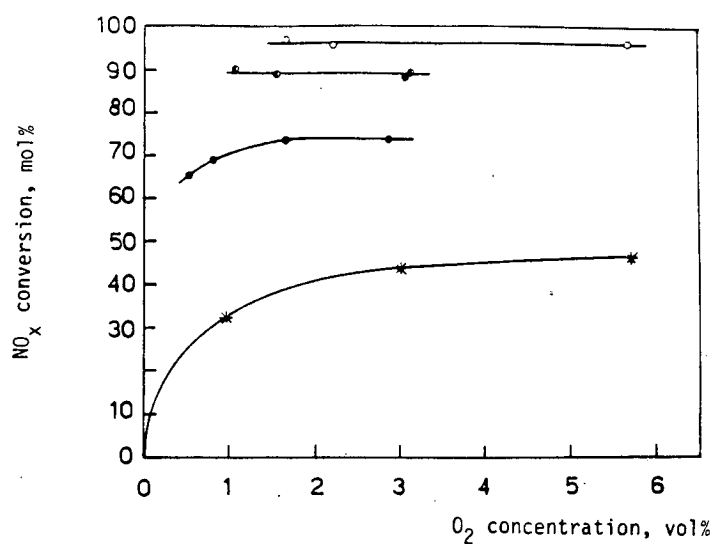


Fig. 10. Effect of oxygen concentration in feed on NO_x conversion at 350°C for NO₂/NO ratios: 1.0 (○); .66 (●); .36 (●); 0.0 (*)

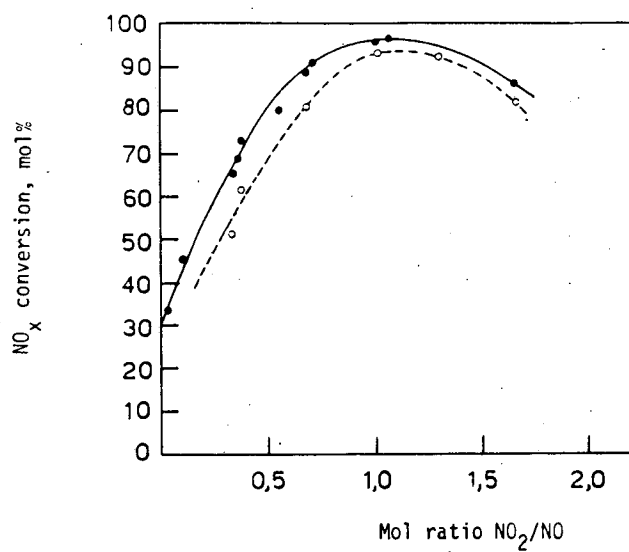


Fig. 11. Effect of NO₂/NO ratio in the feed on the catalytic activity of E-202 catalyst at reaction temperatures: 300°C (o) and 350°C (●).

Effect of the Phosphorus Content

The presence of phosphorus in the composition of the catalyst causes changes in the activity, as shown in Figure 12, where the catalytic activity (as in moles of NO_x converted per minute and gram of catalyst) are plotted as a function of the phosphorus content (given in weight percentage) for the different reaction temperatures.

The decrease in catalytic activity can be interpreted as due to the loss of area with H_3PO_4 (see Figure 2). Therefore, one must compromise between catalytic activity and crushing strength.

The phosphorus content selected was equivalent to that in catalyst E 111, that is close to 15%, due to the fact that this catalyst exhibited acceptable hardness and that the global conversion of NO_x was 90%. Thus, the catalysts have both the strength and the catalytic activity considered useful in the industrial applications.

Effect of the Vanadium Content

In Figure 13 the values of the global conversion of NO_x were plotted as a function of the vanadium content for catalysts of series WO.

It is observed that when the vanadium content is lower than 2%, the catalytic activity is highly dependent on the amount of vanadium present, but when the vanadium concentration is higher than 2% the global conversion of NO_x remains constant.

Effect of the Tungsten Content

Conversely, the amount of tungsten in the catalyst does not seem to have an appreciable influence on its activity. As Figure 14 shows, the level of global conversion of NO_x does not undergo great changes in the range of 0 to 10% tungsten. At 430°C the level of conversion is maintained around 92-93% and at 350°C there appears to be a small increase in the global NO_x conversion when small amounts of tungsten are present.

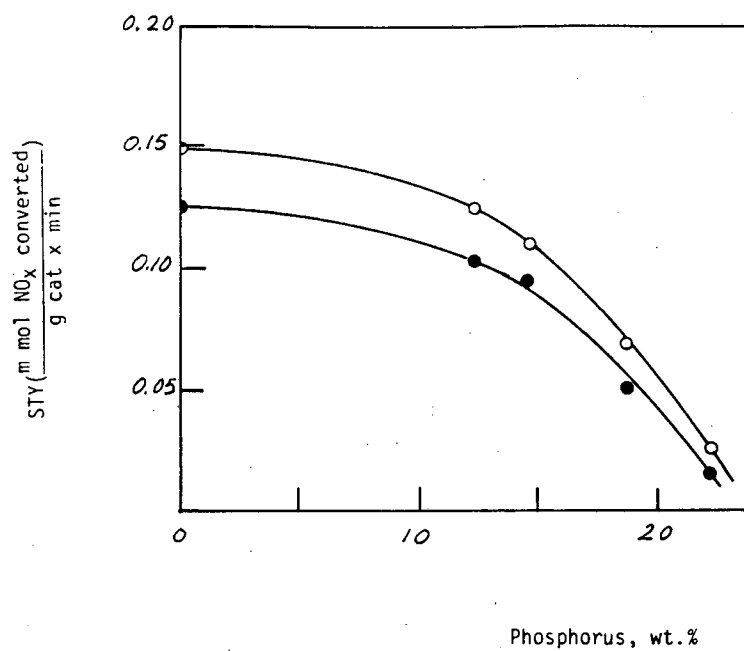


Fig. 12. Influence of phosphorus content on the catalytic activity of series "P" catalysts. Reaction temperatures 350°C (o) and 430°C (●).

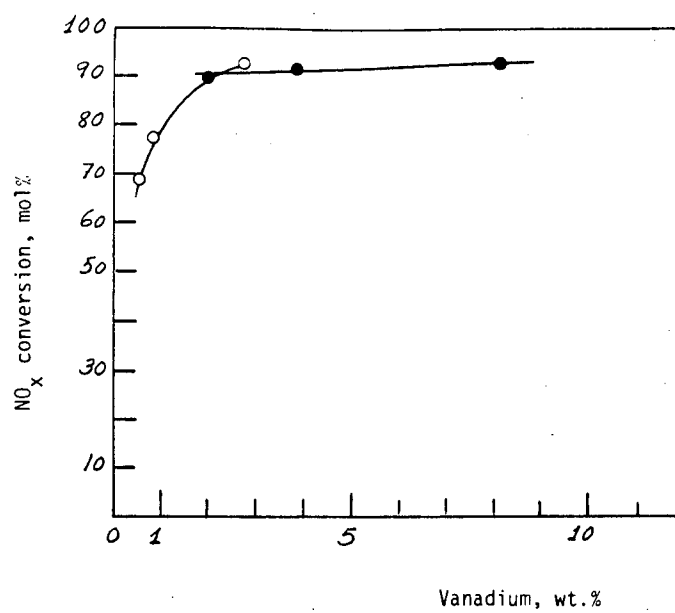


Fig. 13. Effect of the vanadium content on the global conversion of NO_x at 350°C for catalysts of series "W0" (●) and "W5" (○).

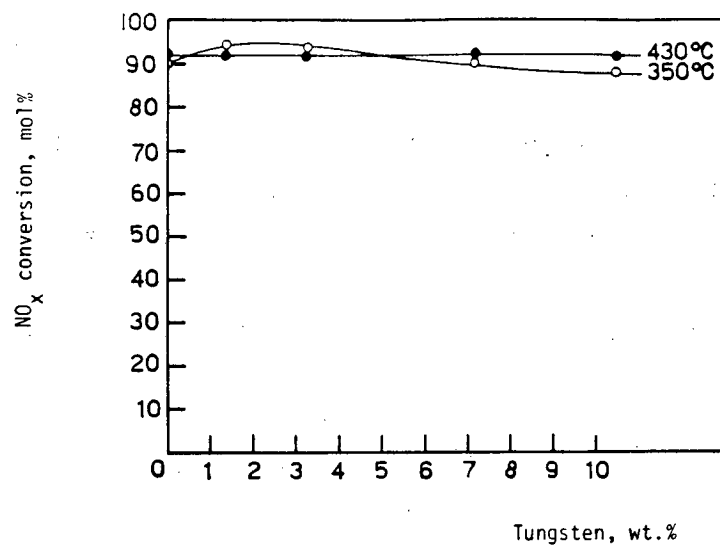


Fig. 14. Effect of W content on the global conversion of NO_x for catalysts of series "V5" at 350°C (o) and 430°C (●).

Since an increase of the tungsten content increases the strength, it seems convenient to add this component to the catalysts in order to obtain a superior catalyst from the point of view of its mechanical properties.

Effect of the V/W Ratio and of the Sulfates

In order to determine the desirability of washing the original paste in order to eliminate sulfates and also to determine the correct amount of W, catalytic activity of the catalysts of series "S" (without sulfate) and "C" (with sulfate) was measured. The results are plotted in Figure 15 as catalytic activity per gram of catalyst versus V/W ratio in the catalyst.

As a general trend, catalysts of series "C" are slightly more active than catalysts of series "S".

This difference in activity between the two series could be explained on the basis of the specific surface of these two series, see Figure 5. As a matter of fact, catalysts of series "C" have a specific surface slightly higher than the equivalent ones of series "S".

Therefore, it is clear that it is not desirable to wash the paste in order to eliminate sulfates. The catalysts must be prepared from the original paste, avoiding manipulation steps that increase production costs.

According to the results given in Figure 15, the catalytic activity per gram of catalyst decreases progressively when the tungsten content increases.

Analysis of the results of global conversion of NO_x (at constant volume: 4.5 ml), given in Figure 16, shows a maximum in activity at a V:W ratio of 8:2.

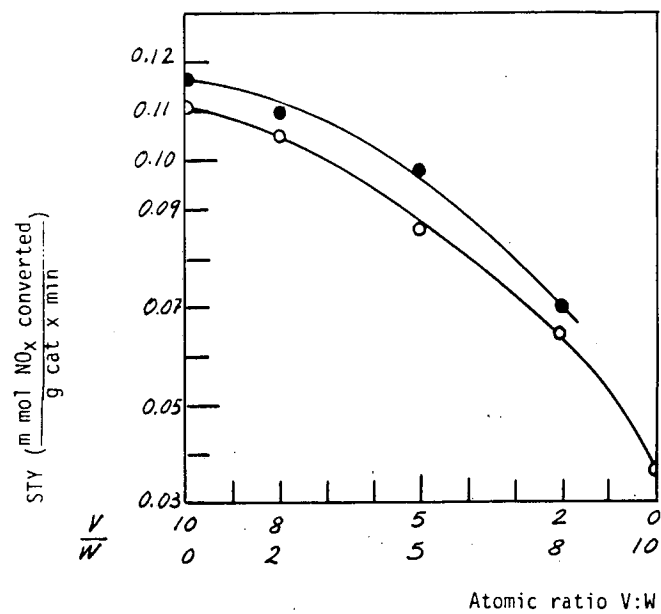


Fig. 15. Effect of the V:W atomic ratio on the activity of catalysts of series "C" (with sulfate) (●) and of series "S" (without sulfate) (○) for the atomic ratio Ti:(V+W)=90:10.

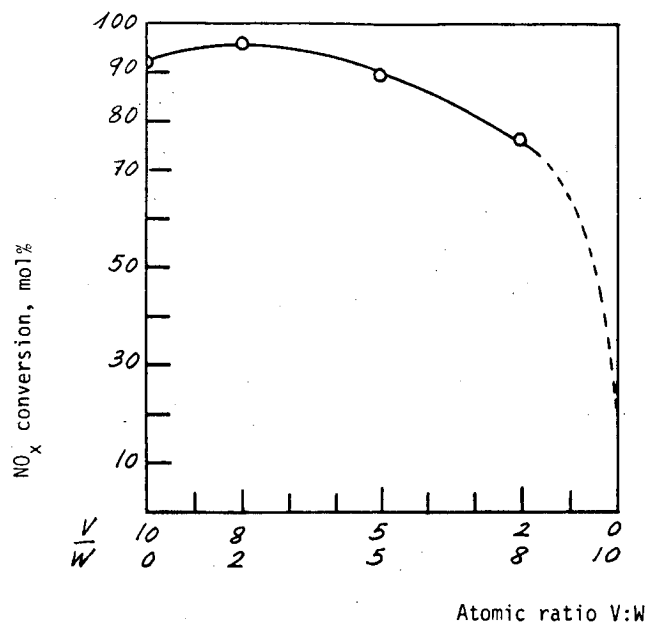


Fig. 16. Effect of the V:W atomic ratio on the global conversion of NO_x of series "C" catalysts (with sulfates) at 350°C.

The difference between the two activity plots is due to the difference in apparent density between catalyst E 201 (without tungsten) and the other catalysts in the series which contain tungsten (see Table 11).

A compromise is again required between the mechanical characteristics of the catalyst and its catalytic activity; the introduction of higher tungsten percentages than those corresponding to a ratio $V/W = 1$ produces an increase in hardness but a decrease of catalytic activity parallel to the decrease in surface area.

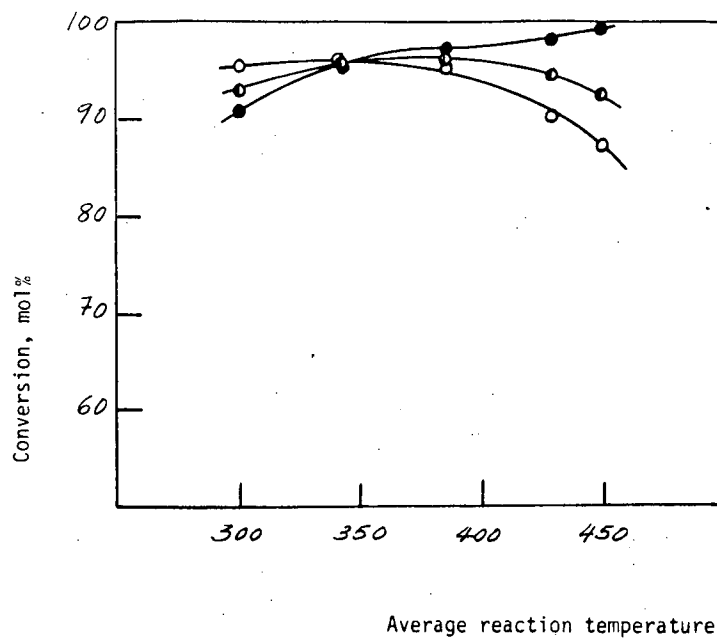
On the basis of these results, it was decided that E 218 (E 90.8.2. C3T) is the catalyst having the most suitable properties for industrial use.

Behavior of the Selected Catalyst

Catalyst E 218, the physical characteristics of which are given in Table 11, has the best properties, both mechanical and catalytic, of the catalysts tested in this study.

Figures 17 and 18 show the change in conversion of NO , NO_2 , and NO_x with the selected catalyst. The global conversion of NO_x at the operating conditions previously described is higher than 90% through the whole range of commercial interest.

By comparing these results with those obtained at the same conditions with the catalyst called "commercial standard," it is clear that the catalyst described in this work has a higher activity than the "commercial standard," through the entire range of temperatures studied, and therefore can be considered as a suitable catalyst to be optimized.



Operating Conditions:

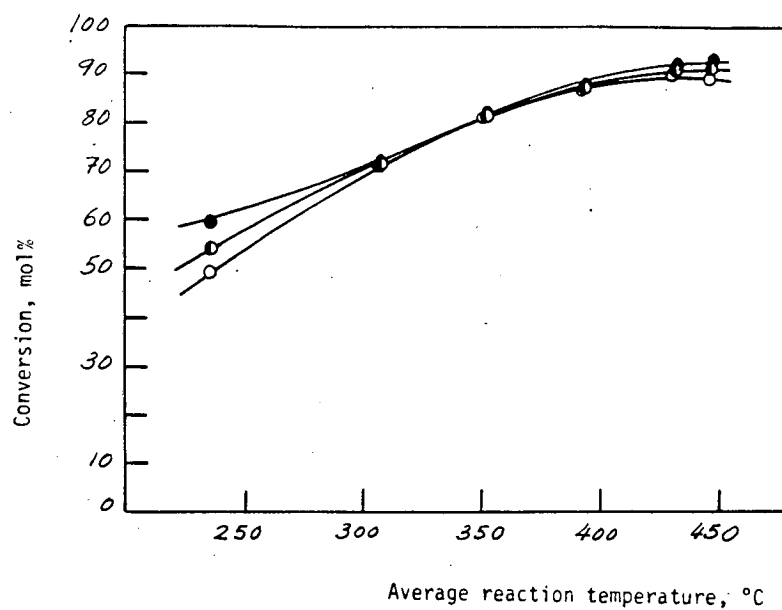
GHSV = 40.000 h⁻¹

Feed composition:

NO_x : 3000 vpm (NO: 1500 vpm,
NO₂: 1500 vpm)
NH₃ : 3300 vpm
O₂ : 2-3 %vol.
N₂ : balance

Catalyst: E-21C (E.90.8.2 C3T)

Fig. 17. Effect of reaction temperature on activity of catalyst E-21C. NO₂ (●); NO_x (●); NO (○).



Operating Conditions:

GHSV = 40.000 h⁻¹

Feed composition:

NO_x : 3000 vpm (NO: 1500 vpm,
NO₂: 1500 vpm)

NH₃ : 3300 vpm

O₂ : 2-3 %vol.

N₂ : balance

Catalyst: Sud=chemie

Fig. 13. Effect of reaction temperature on activity of a commercial catalyst. NO₂ (●); NO_x (●); NO (○).

C.6 CATALYST ACTIVITY (Power Plants)

The same types of catalysts have been tested for the elimination of nitrogen oxides in the tail gas of thermal power plants.

The main difference in the treatment of the two antipollution processes (HNO_3 plants and thermal power plants) is the composition of the gas phase to be treated.

This composition and the conditions are as follows:

Composition	HNO_3 Plants	Thermal Power Plants (coal)
NO_x ppm	2000-4000	200-1200
NO/NO_2	1/1	10/1
O_2 % vol	2-3	1-5
H_2O % mol	1-2	10-20
SO_x ppm	-	300-800
CO_2 % mol	-	10-15
Ash mg/ Nm^3	-	10,000-20,000
Conditions:		
Pressure (atm)	3-7	1
Temperature $^{\circ}\text{C}$	200-500	350
Vol. of gases Nm^3/h	$(5-50) \times 10^3$	$(100-2000) \times 10^3$

The previously used operating conditions have therefore been changed. Experiments were performed at conditions similar to those of the tail gases of coal thermal power plants.

Variables studied have been:

- Effect of the presence of SO_2 in the feed.
- Influence of the concentration of H_3PO_4 used during the extrusion process.
- Influence of the treatment temperature of the catalyst.
- Influence of the composition of the catalyst (ratio V/W).

Results obtained are presented below along with the most important conclusions.

Effect of SO_2

During the preliminary experiments performed at operating conditions similar to those needed for the treatment of tail gases from thermal power plants, the temperature of reaction and the concentration of SO_2 were changed.

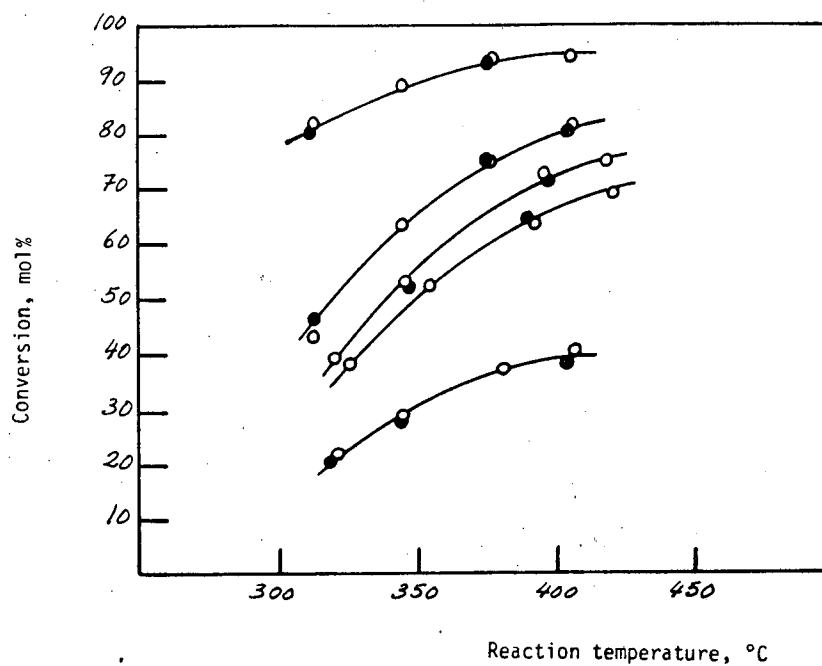
The results obtained are shown in Figure 19. These results clearly indicate that the inclusion of SO_2 in the feed has no appreciable effect on the catalytic activity of these solids for the reduction of NO_x in the range of temperatures considered.

In view of this fact, it was decided to carry out the experiments without SO_2 in the feed in order to avoid secondary problems, such as the possible formation of ammonium sulphate and bisulphate or the corrosion of some sensitive elements of the analytical systems.

Effect of H_3PO_4

In section C.4 it was shown that H_3PO_4 causes an appreciable change in the physical properties of the catalysts. These physical changes have an important influence on the catalytic activity in the sense that catalytic activity decreases when phosphorus content increases.

Figure 19 shows that the "commercial standard" catalyst is more active than all the catalysts of series "C". This is mainly due to the fact that the catalysts of series "C" have a high concentration of phosphorus ($\approx 15\%$), because if we compare the activity of the



Operating conditions:

GHSV = 18.000 h⁻¹

NO_x = { NO = 1200
NO₂ = -

NH₃ = 1400 ppm

O₂ = 3 %vol.

●SO₂ = 700 ppm ; ○SO₂ = 0 ppm

Fig. 19. Comparison of the catalytic activity of series "C3 500" catalysts and of the commercial catalyst as a function of reaction temperature.

"commercial standard" catalyst with the activity of E 214 (E 90.8.2.S-T) it is clear (Figure 20) that E 214 is more active than the "commercial standard" catalyst.

This negative influence of H_3PO_4 is also shown by the results given in Figure 21, where conversion of NO (at a reaction temperature of $350^\circ C$ and $GHSV = 72.000\ h^{-1}$) versus phosphorus concentration was plotted for catalysts of the series "P". The decrease of the catalytic activity due to the H_3PO_4 parallels the decrease in surface area. Therefore, the addition of phosphorus to the catalyst should be limited to the smallest amount necessary to obtain a material of sufficient hardness.

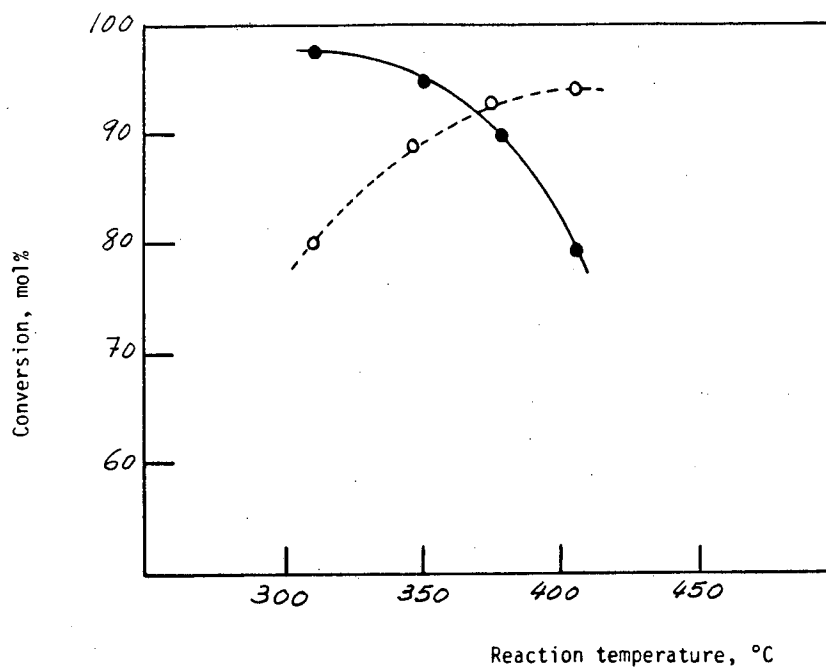
Effect of Pretreatment Temperature of Catalysts

Catalytic activity of series "T" and series "C5" catalysts has been measured at the above described conditions. The results obtained are presented in Figures 22 and 23.

In these graphs it is shown that catalytic activity increases with increasing pretreatment temperature between 500 and $700^\circ C$ but drops abruptly above this temperature.

The increase of activity with pretreatment temperature could be explained by changes in the porosity of the solids (increase of pores with $r > 500\ \text{\AA}$); the explanation of the decrease of activity when pretreating the catalyst at $800^\circ C$ requires the consideration of other physicochemical factors as, for example, a change of the structure of TiO_2 (anatase \leftrightarrow rutile), a change in the vanadium species at the surface, etc. To do this the complete characterization of this series of catalysts is required.

However before selecting a catalyst for this process, one needs to study the influence of other preparation variables such as the



Operating conditions:

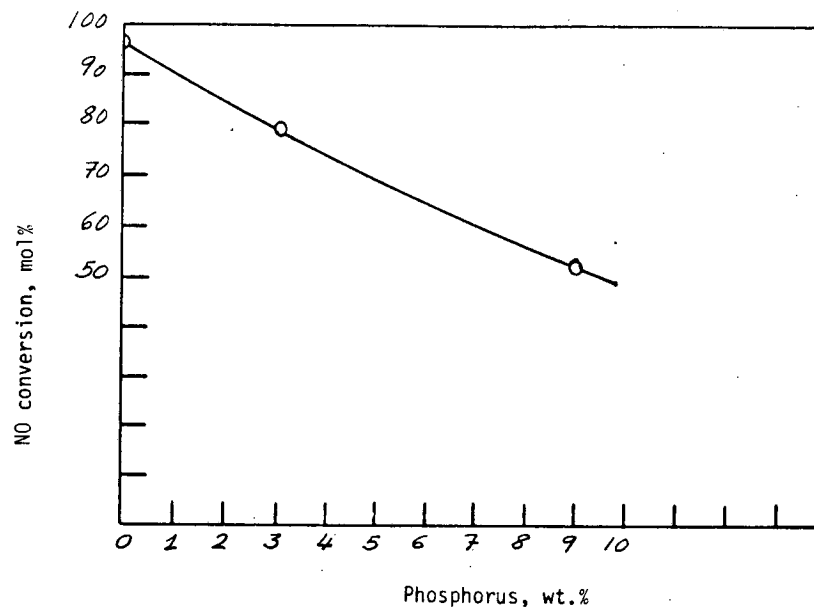
GHSV = 18.000 h⁻¹

NO_x = { NO = 1200
 NO₂ = -

NH₃ = 1400 ppm

O₂ = 3 %vol.

Fig. 20. Comparison of the catalytic activity of the commercial catalyst (○) with catalyst E-214 (E 90.8.2.500T) (●) as a function of reaction temperature.

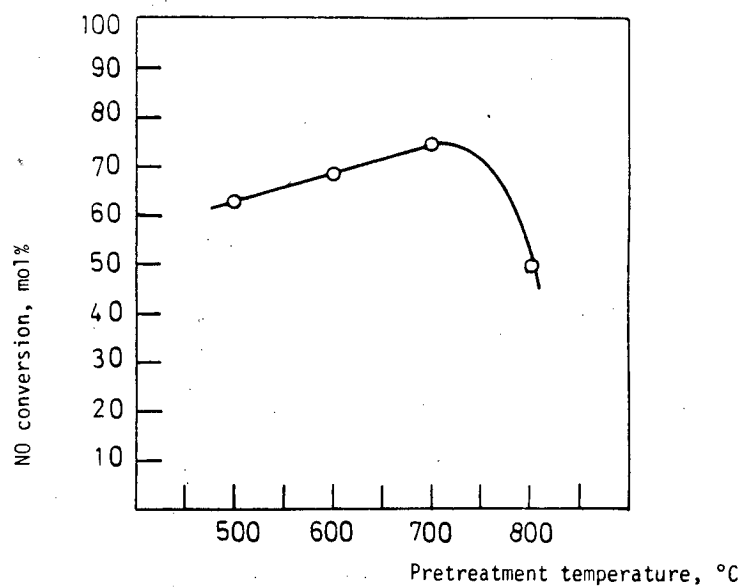


Operating conditions:

GHSV = 2000 h^{-1}

Feed composition: NO : 1200 ppm
NH₃ : 1300 ppm
O₂ : 3 % vol

Fig. 21. Effect of phosphorus content on activity of catalysts of series "C" at 350°C.

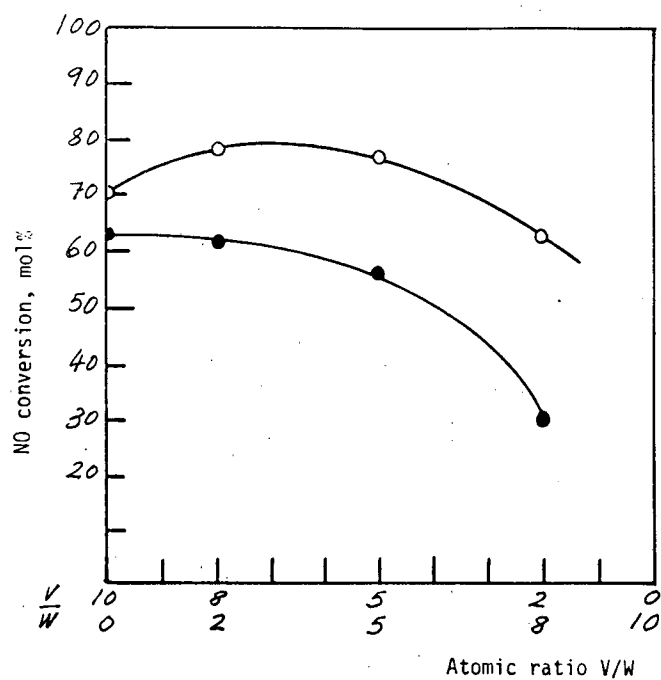


Operating conditions:

GHSV = 40.000 h⁻¹

Feed composition: NO = 1100 ppm
NH₃ = 1100 ppm
O₂ = 3% vol.

Fig. 22. Effect of pretreatment temperature on the catalytic activity of series "T" catalysts (E.90.8.2.CST) at 350°C.



Operating conditions:

GHSV = 40.000 h⁻¹
 Reaction temp. = 350°C
 Feed composition: NO = 1100 ppm
 NH₃ = 1200 ppm
 O₂ = 3% vol.

Fig. 23. Catalytic activity of series "C5" catalysts pretreated at 700°C (o) and at 500°C (●).

utilization of other binders (possible substitutes for H_3PO_4) or the treatment with oxalic acid in order to reduce V^{5+} to V^{4+} with the aim of improving its catalytic properties.

Effect of Sodium Content

The activity of two catalysts (E 341 without Na and E 352 with Na) was measured using the same experimental conditions (GHSV = $40,000 \text{ h}^{-1}$, reaction temperature: 350°C) both in the system $\text{NO} + \text{NH}_3 + \text{O}_2$ (thermal power stations) and in the system $\text{NO} + \text{NO}_2 + \text{NH}_3 + \text{O}_2$ (HNO_3 plants). The results, given below, show that the catalyst containing Na was a little less active than the catalyst without Na.

Catalyst	Conversion	
	$\text{NO} + \text{NH}_3 + \text{O}_2$	$\text{NO} + \text{NO}_2 + \text{NH}_3 + \text{O}_2$
E 341	57%	92.5%
E 352	52%	89.0%

C.7 CATALYST SELECTION AND LIFE

Selection of a Catalyst

The factors which influence the two parameters to be optimized (catalytic activity and crushing strength) require the adoption of a compromise in order to obtain the best catalyst for this process.

It is believed that the best catalyst must have the smallest possible phosphorus content, which permits an acceptable hardness (crushing strength $\geq 5 \text{ K}_p$), in order to obtain high catalytic activity.

According to the previously shown experimental data, the atomic ratio W:V must be between 1 and 2, the V content must be higher than 2% ($\text{Ti:V} \leq 95.5$) and the phosphorus content must be lower than 12% ($\text{F} \geq 5$).

On this basis two new catalysts were prepared, E-313 (E.87.5.8 C7,5T 700) and E-318 (E.87.5.8 C10T 700).

Figure 24 shows the change in the NO conversion and the residual NH_3 concentration, obtained with these catalysts when changing the proportion of NH_3 in the feed. The reaction takes place at 350°C and a space velocity of $40,000 \text{ h}^{-1}$. From this figure it can be seen that the catalyst with the lowest phosphorus proportion (E-318) is more active than the one having a dilution factor $F=7.5$ (E-313). Since the crushing strength of catalyst E-318 is 7 K_p , it is assumed that this catalyst could be used industrially, if it is possible to decrease the proportion of NH_3 in the exit gases and increase the degree of NO conversion per pass.

These two objectives can be achieved by decreasing the space velocity, because, as it is shown in Figure 25, at values of weight of catalyst/flow $\geq 5 \times 10^{-5} \text{ h}$ ($\text{GHSV} \leq 20,000 \text{ h}^{-1}$), values of NO conversion are greater than 90%, with a residual concentration of NH_3 of less than 100 ppm.

Moreover, it is possible to obtain a lower NH_3 residual concentration by decreasing the NH_3/NO_x in the feed below unity. For example, at $20,000 \text{ h}^{-1}$, with a ratio NH_3/NO_x in the feed equal to 0.9 the concentration of NH_3 residual is lower than 5 ppm; but the NO_x conversion obtained is 88%.

The consideration of these two parameters (ratio NH_3/NO_x and GHSV), allows determination of the amount of catalyst required to obtain the degree of NO_x elimination to fit the requirements of today's regulations and the concentration of residual NH_3 appropriate to avoid the formation of ammonium salts.

Figure 26 shows the results obtained at $20,000 \text{ h}^{-1}$ with this catalyst when changing the concentration of NH_3 in the feed.

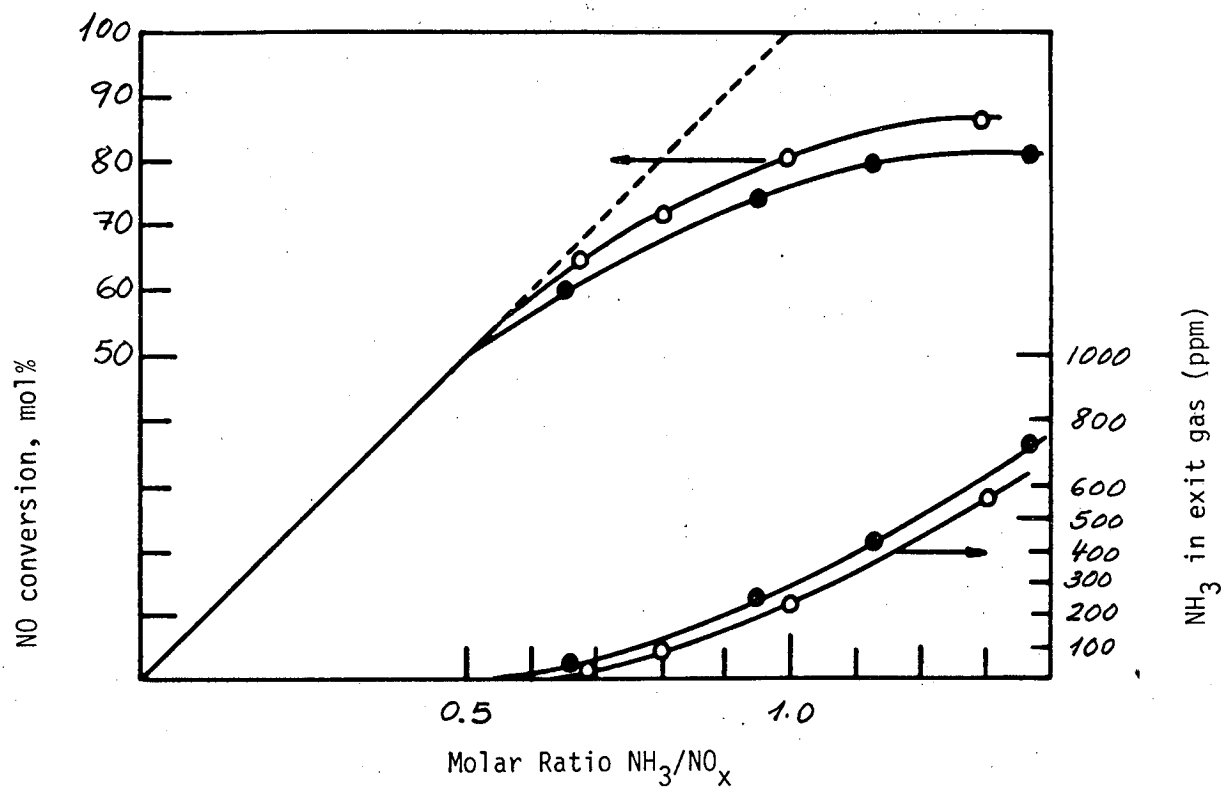


Fig. 24. Effect of mol ratio NH_3/NO_x on NO conversion and NH_3 content of exit gas for catalysts E-313 (●) and E-318 (○)

GHSV = $40,000 \text{ h}^{-1}$

Reaction Temperature: 350°C

Feed Composition: NO : 1100 ppm
 NH_3 : variable
 O_2 : 3 vol%

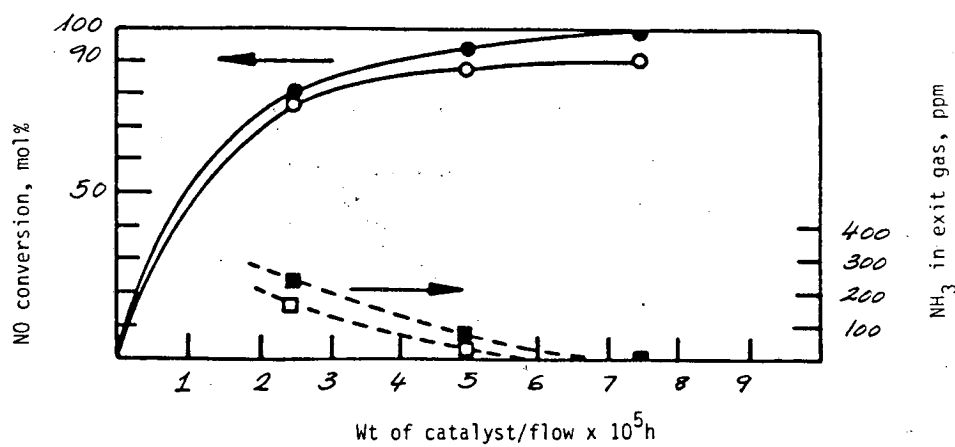


Fig. 25. Effect of contact time and of NH₃/NO_x mol ratio in feed on NO conversion and NH₃ concentration in the exit gases. NH₃/NO_x : 1.0 (● and ■); 0.9 (○ and □)

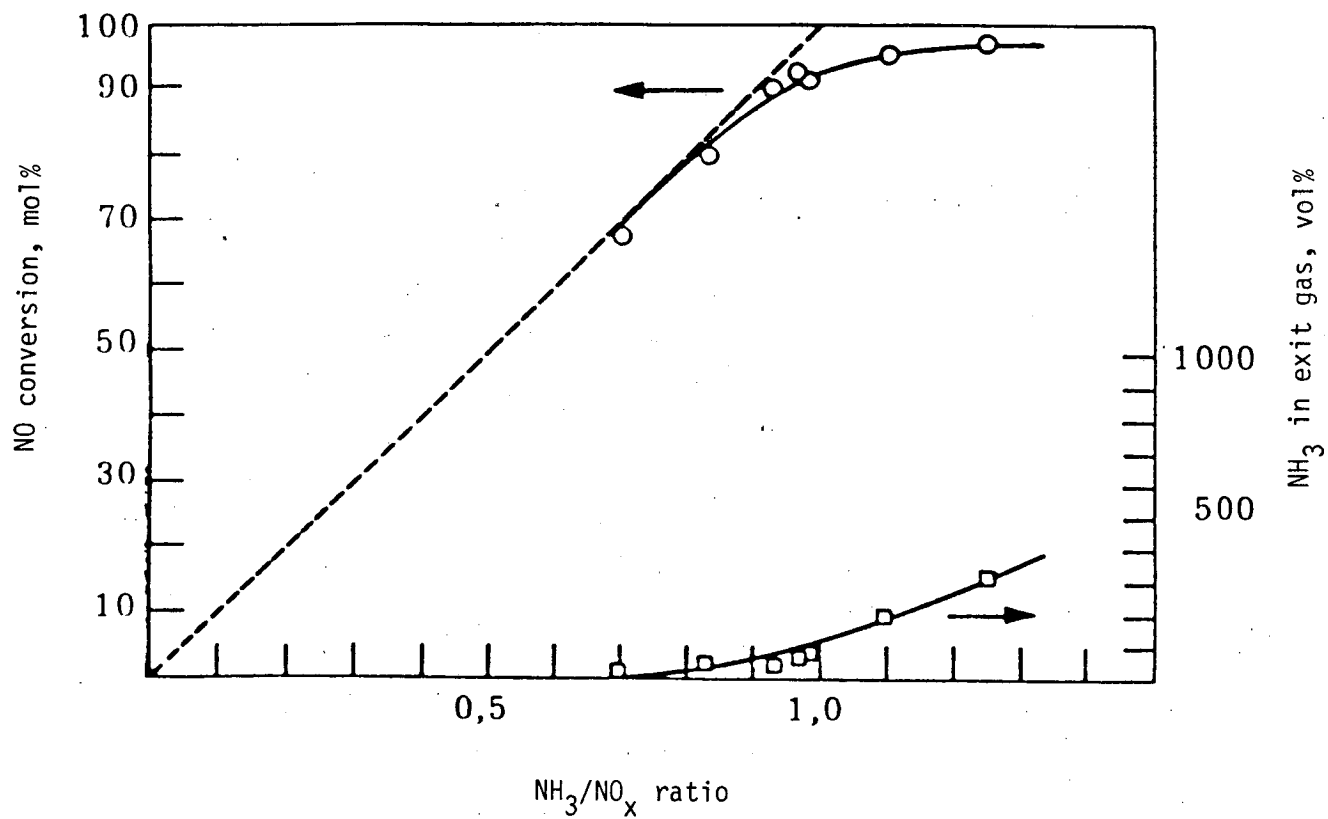


Fig. 26. Effect of NH_3/NO_x ratio in the feed on NO conversion (o) and on concentration of NH_3 in the exit gas (\square).

It can be seen that when the NH_3/NO_x ratio in the feed is equal to 0.8, NO_x conversion is on the order of 80% and the NH_3 residual concentration is practically nil.

Conclusions

The results obtained on a laboratory scale, with the selected catalyst, can be considered satisfactory, because NO_x conversions greater than 80% can be obtained at a relatively high space velocity ($20,000 \text{ h}^{-1}$) with a NH_3 residual concentration which is practically nil. Catalysts described in the literature operate at space velocities of 3,000 to $6,000 \text{ h}^{-1}$ and therefore are needed in amounts which are between 4 and 6 times higher.

Even though the behavior of this catalyst has been satisfactory, the final development of an industrial catalyst would be much improved if its shape would allow the gas circulation in parallel flux; e.g., within a structure of tubes, planes or monoliths (honeycomb). Moreover, even though H_3PO_4 is a good binder for this type of solids, the possibility of using a different binder with less effect on the catalytic activity should be studied.

Life Tests

Three catalysts (P-214, E-318, and the commercial catalyst, CC) were tested under the conditions shown in Table 19 for 188 continuous hours each. The results are presented in Table 19 and Fig. 27 and indicate that P-214 and CC are about equivalent after about 60 hours of operation as far as NO conversion is concerned. E-318 has a lower NO conversion, however, as previously indicated, is considerably harder. All catalysts show an initial activity decline. CC has the smallest activity decline but starts at a lower initial activity than the other two catalysts. All catalysts seem to reach a steady state activity after about 80 hours.

Table 19

NO Conversion

350°C; GHSV: 20,000 hr⁻¹; NO: 1100 ppm; O₂: 3.0 vol%;
 NH₃: 1100 ppm; SO₂: 5000 ppm

	$\frac{12 \text{ hrs.}}{P-214 \quad E-318}$		$\frac{24 \text{ hrs.}}{P-214 \quad E-318}$		$\frac{48 \text{ hrs.}}{P-214 \quad E-318}$		$\frac{96 \text{ hrs.}}{P-214 \quad E-318}$		$\frac{140 \text{ hrs.}}{P-214 \quad E-318}$		$\frac{188 \text{ hrs.}}{P-214 \quad E-318}$	
NO Conversion mol%	96	90	86		88	80	84		85	74	83	
NH ₃ , ppm exit	20	60	40		25	100	43		26	120	42	
SO ₃ , ppm exit	0	0	0		0	0	0		0	0	0	

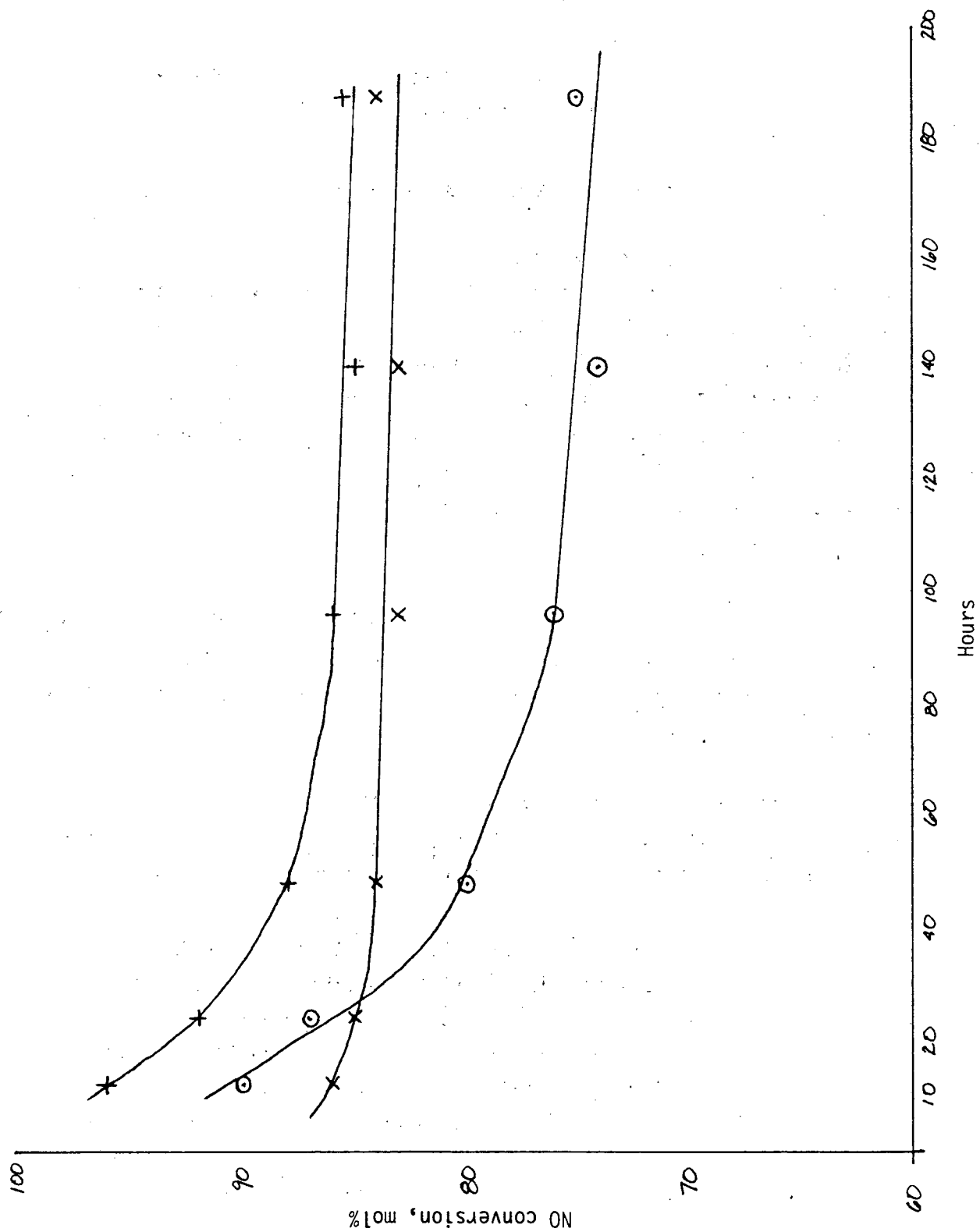


Fig. 27. Life studies of catalysts E-318 (o); P-214 (+); and the commercial catalyst (x).

No SO_2 is produced in any of the exit gases from SO_2 and O_2 in the feed. Ammonia breakthrough in the exit gases is smallest for the P-214 and largest for E-318 with CC being intermediate.

C.8 ADSORPTION AND SPECTROSCOPIC MEASUREMENTS AND MECHANISTIC CONSIDERATIONS

Adsorption and Infra-Red Studies

Adsorption measurements of NO on titania and on various $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts show that titania adsorbs NO to a substantial extent and that catalysts containing V have appreciably lower adsorption, probably due to surface titanium phosphate formation. The 90-2-8-C catalyst containing no P shows the highest adsorption capacity. The difference between it and the pure titania sample used may be due to different titania sources (Fig. 28). Fig. 29 shows that reduction with H_2 of vanadia-tungsten-titania catalysts shows a maximum at a reduction temperature of about 300°C .

Other experiments have shown that pure V_2O_5 does not sorb NO, while lower valent vanadium oxides do sorb NO. Another explanation for the high NO adsorption of the reduced CC catalyst may be the ability of lower valent vanadia to sorb NO.

Infra-red spectra of NO or of NO_2 on the 9028-C catalyst were obtained. They show that different chemisorbed species are present and the relative concentration changes with temperatures and partial pressure.

Effect of Temperature of Pretreatment on the Surface Composition of Catalysts Containing P

Surface composition of V-Ti-O catalysts as a function of phosphorus content and the pretreatment temperature was studied using x-ray photon spectroscopy (XPS). Three samples with different phosphorus content were selected. They were identified as $\text{P}(x)\text{-VTi}_T$ where x had the values 0.0, 11.5 and 14.8% and T is the pretreatment temperature in

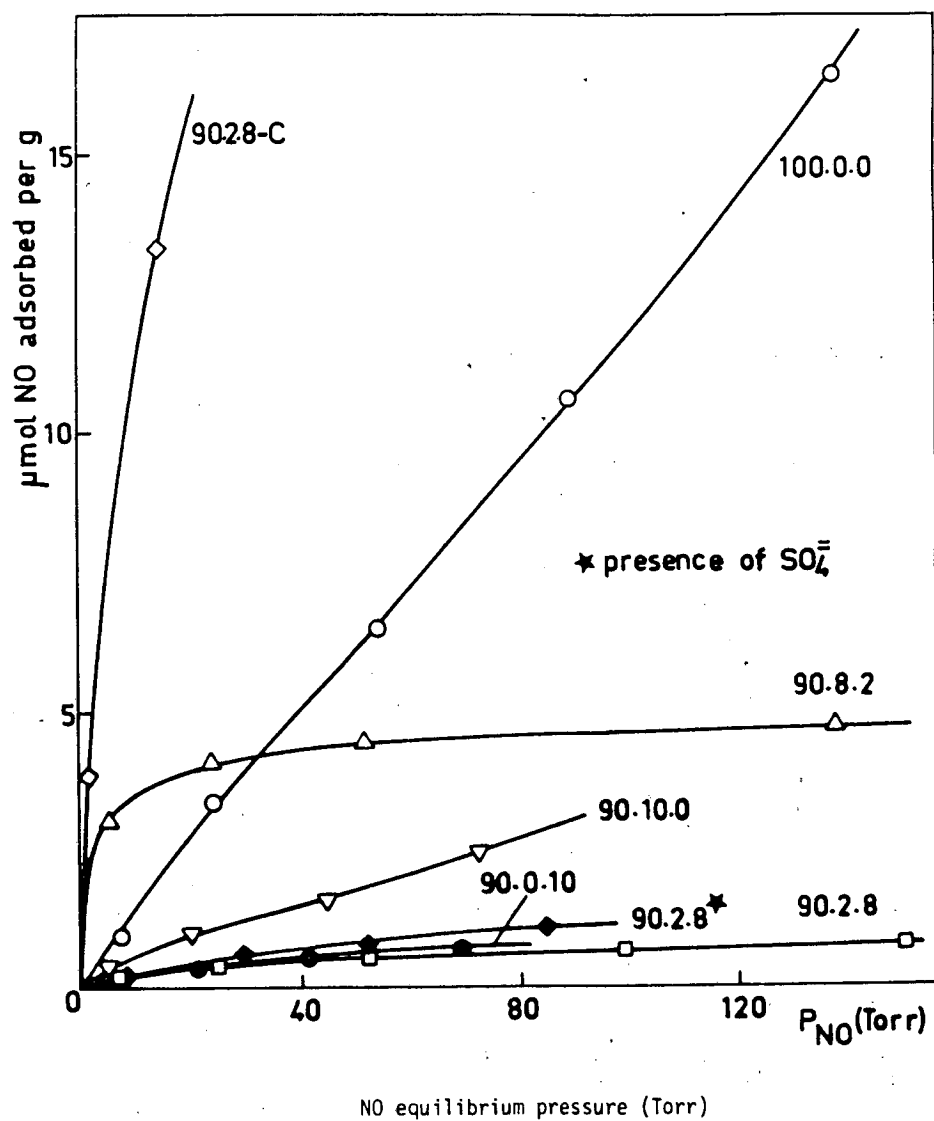


Fig. 28. Adsorption isotherms of NO for catalysts.

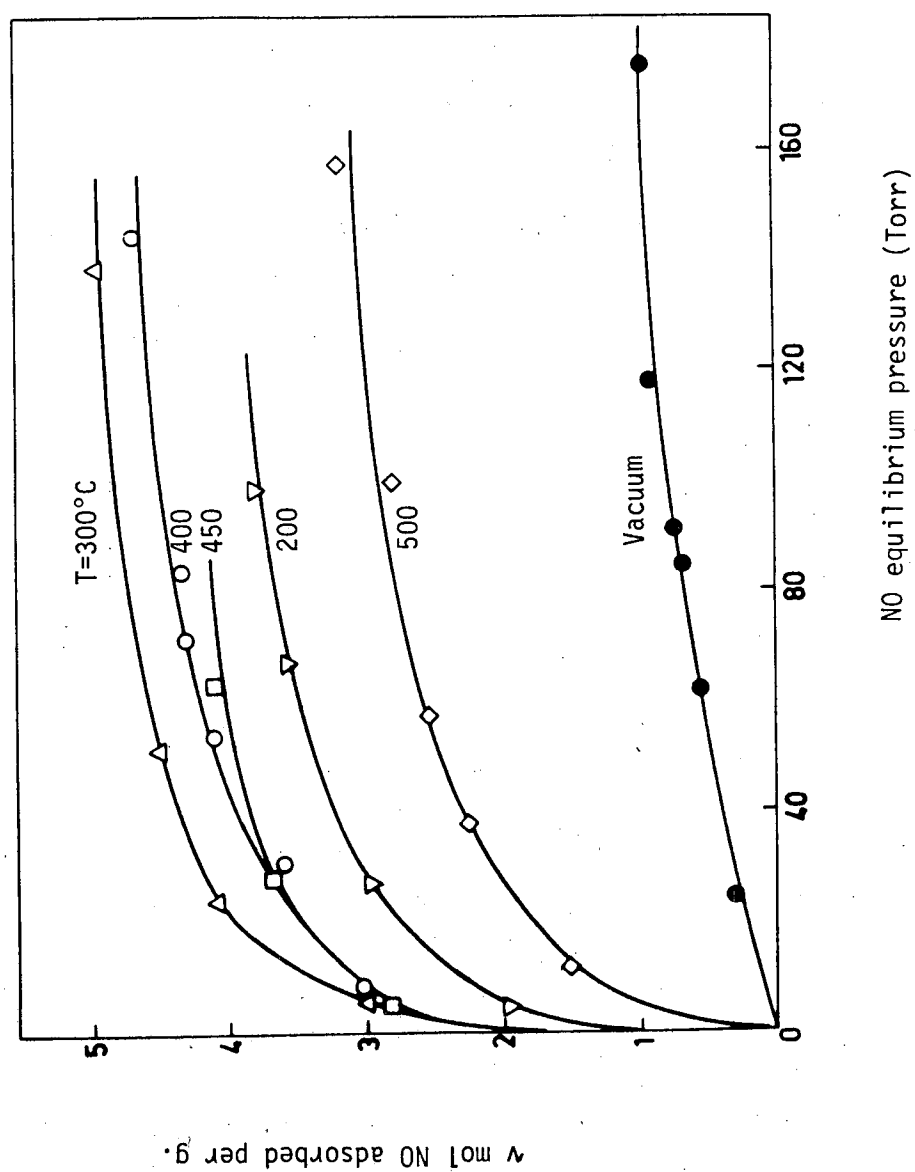


Fig. 29. Adsorption isotherms of NO at room temperature on catalyst E.90.8.2S, prereduced at different temperatures and treated in vacuum.

$^{\circ}\text{C}$. These samples were heated to 500°C in air. In addition samples containing phosphorus were also heated to higher temperatures (700 and 800°C).

For each catalyst the levels O_{1s} , Ti_{2p} , V_{2p} , P_{2p} , and W_{4d} were measured by an accumulation adequate to obtain a good ratio of signal to noise. From the peak areas, the number of accumulations and the sensitivity factors reported in the literature for each emission, some atomic ratios were calculated. These ratios are summarized in the following table.

Table 20
Surface Atomic Ratios from XPS Spectra

Catalysts	P(%)	V(%)	O/Ti	P/V
P(0)-VTi ₅₀₀	0.00	61.22	5.31	0.00
P(11.5)-VTi ₅₀₀	35.1	0.26	7.69	138
P(14.8)-VTi ₅₀₀	35.7	0.64	6.15	56
P(11.5)-VTi ₇₀₀	30.8	0.58	6.03	53
P(11.5)-VTi ₈₀₀	42.3	0.42	4.35	101
P(14.8)-VTi ₇₀₀	41.5	0.83	2.50	50

The table shows that the surface atomic ratio strongly depends both on phosphorus content and pretreatment temperature. The most important result is the decrease in V content due to the phosphorus incorporation into the base preparation, P(0)-VTi. However, this decrease is not proportional to the phosphorus content because it slightly increases in the sample richest in phosphorus, P(14.8)-VTi₅₀₀. Comparing the surface content of vanadium in the same sample heated at increasing pretreatment temperature, it is evident that there is a increase in V content in the samples heated at 700°C . When heating the sample from 700 to 800°C , the surface content of V declines.

The surface concentrations of P and V expressed as the atomic ratio P/V has been calculated and plotted as a function of the

temperature in Figure 30. These ratios are very high; the experimental values of P/V are one or two orders higher than could be expected from stoichiometric compounds of P and V. The quick drop in the P/V ratio in sample P(11.5)-VTi_T when increasing the pretreatment temperature to 700°C, seems to indicate that the formation of a type of vanadium (and possibly titanium) phosphate is in progress at this temperature interval. This result is not surprising because an increase in temperature is favorable for such a reaction in solid state, involving diffusion of reactants and products and chemical transformations. The following increase of P/V ratio at pretreatment temperature of 800°C on the same sample indicates either an increase in P or a decrease in V at the surface. The first hypothesis should be excluded due to the fact that during previous thermal treatments the P was able to react with V and Ti in several layers below the surface. The second hypothesis is more likely. There are several references in the literature on the facility of V⁴⁺ ion to form a solid solution V_xTi_{1-x}O₂, with rutile structure, when the pretreatment temperature is higher than 650°C.

XPS, Auger, and TDS Studies

A considerable amount of literature dealing with the selective catalytic reduction of nitrogen oxides can be found due to the evident interest of this reaction for the air quality standards. Among the catalysts tested, supported vanadium oxides seem to be preferred for improving the NO_x + NH₃ + O₂ reaction. However, differences in the performance of the supported vanadium catalysts have been observed depending on differences of the support [1]. Although a few mechanisms for the NO + NH₃ reaction have been proposed [2-7], the separate effects of the active phase and the support and the effects that may be derived from their mutual interaction have not been well studied in the literature.

In general, the reduction of the supported V⁵⁺ species is assumed, although the species that reduces the V⁵⁺ site and the

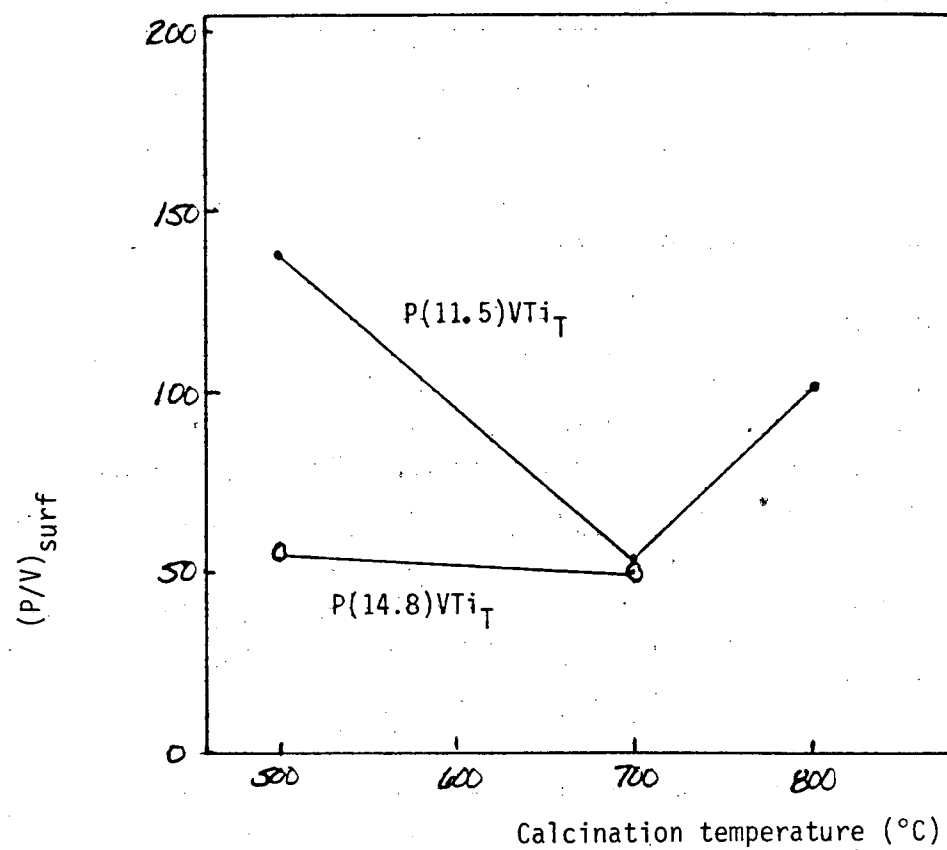


Fig. 30.

mechanism through which the reduction takes place is still speculative. Some data have previously been reported that discard the possibility of $\text{NH}_3\text{-NO}$ adduct formation on $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts suggesting as more likely a redox mechanism in which the reduction of the V^{5+} species takes place by NH_3 which in turn is oxidized. However, much less information had been obtained on the mechanism and the reaction site for the reduction of NO .

In order to obtain information about the mechanism for this reaction the adsorption of NH_3 and NO on pure V_2O_5 samples has been studied by Auger electron spectroscopy (AES) and Thermal Desorption Spectroscopy (TDS). This, in an attempt to understand the differences in behavior, if any, between pure vanadium oxide and supported V^{5+} species. In addition to this, some elementary steps for the $\text{NO} + \text{NH}_3$ reaction on V_2O_5 samples have been enumerated. Further, some questions are currently being investigated concerning the role of the support.

The instrument employed has been previously described [1]. In brief, it consists of a UHV chamber with a built-in high pressure cell which allows switching the sample from the high pressure cell to the UHV system without exposing it to air. The XPS spectra were recorded using a cylindrical mirror analyzer and MgK radiation. For the spectra calibration the $\text{Au}(4f_{7/2})$ line at 83.8 eV and the $\text{Ti}(2p_{3/2})$ at 458.5 eV were used. Referencing the peak positions to the $\text{C}(1s)$ line was avoided due to the disappearance of the carbon signal coming from the sample holder which might cause misleading interpretations. The data treatment of every spectrum included in this report only implies normalizing and shifting due to the charge correction. In the present study a powdered vanadium oxide catalyst (V_2O_5) from Aldrich Chemical Co., 99.999% pure was employed. High purity gases, NH_3 , NO , and O_2 were obtained from Matheson and used without further purification.

The apparatus used for the Auger electron spectroscopy (AES) and

Thermal desorption spectroscopy (TDS) studies is shown schematically in Figure 31. It consists of a stainless steel bell-jar, evacuated to pressures below 5.10^{-9} Torr by a Varian VHS6 diffusion pump, backed by a rotary pump.

The sample holder is part of the high pressure cell (up to 1 atm.). When it is open, the cell exposes the sample to ultra-high vacuum (UHV) for AES and/or TDS analysis, and when it is closed, becomes a part of the reactor used for sample treatments. The sample is pressed against a stainless steel gold coated mesh, and it is in an intimate contact with a chromel-alumel thermocouple. The mesh is then held against a gold foil by two lateral flaps. By passing current through the foil the sample can be heated to the desired temperature.

The Auger electrons were detected by a double-pass cylindrical mirror analyzer (CMA) equipped with a coaxial electron gun (Physical electronics 15-255G). A 6 eV peak-to-peak modulation and a response time of 20 ms were selected while no information is provided on the contrary. The electron gun was always operated at 1kV and 0.8 mA at normal incidence.

Thermal desorption spectroscopy (TDS) studies of the type, exploring stability and reactivity of different gases used in this study have been performed.

For TDS studies, the adsorbate was introduced into the high pressure cell at pressures close to the ones usually achieved under actual industrial conditions (ca. 25 Torr), allowing it to circulate at the temperature chosen (room temperature to 675K) for 15 minutes. After that the sample was cooled down in the adsorbate atmosphere and outgassed in the UHV chamber, at the adsorption temperature, until the system base pressure was achieved. The sample was then heated, under UHV conditions, at a constant heating rate (15K.s^{-1}). A mass spectrometer (UTI 100C) monitors the gas evolution of a given mass, and a plot of the signal

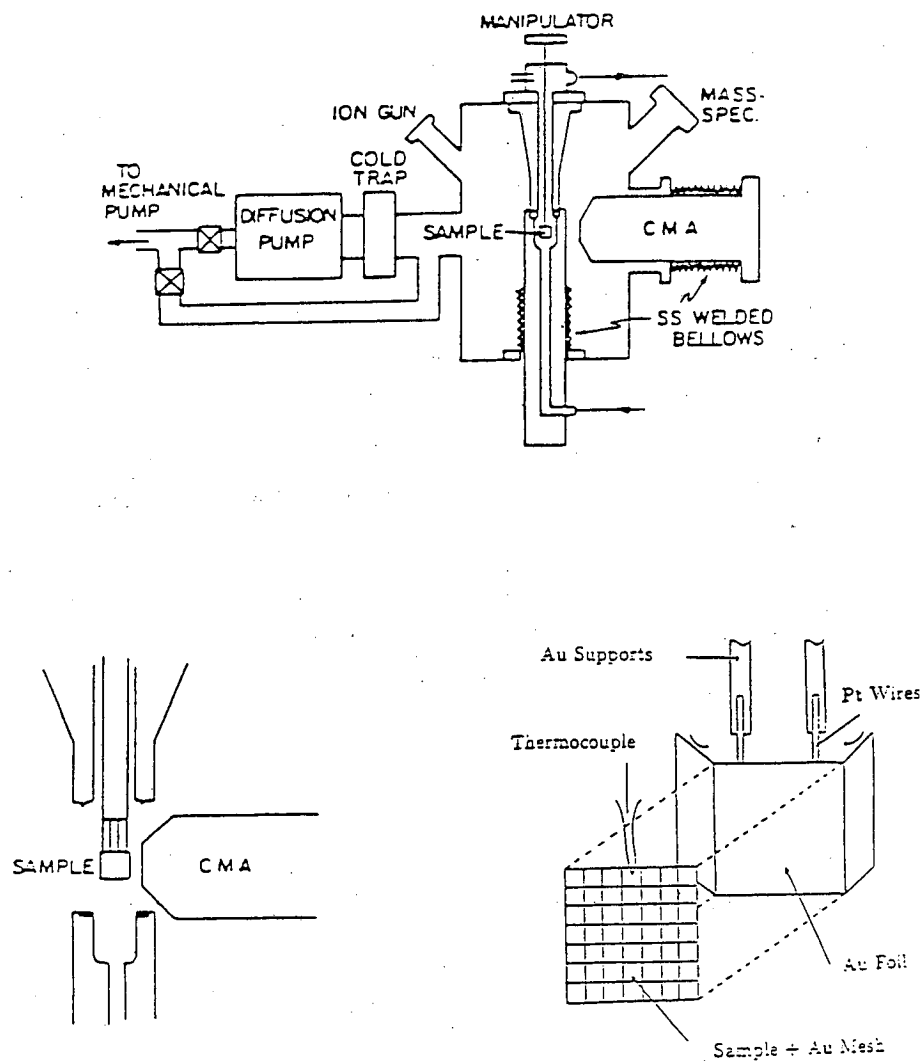


Fig. 31. Apparatus for Auger Electron Spectroscopy and for Thermal Desorption Spectroscopy

intensity versus temperature is generated on an XY recorder (Hewlett-Packard 7044B).

The adsorption of NH_3 and NO has been studied on pure V_2O_5 by AES and TDS. The presence of carbon contamination on V_2O_5 has been described as responsible for the reactivity of thin films of V_2O_5 on gold foils [2]. The formation of CO and/or CO_2 that desorbs at ca. 675K might be responsible for the generation of vacancies on the V_2O_5 surface leaving exposed V^{4+} species that can then react with the adsorbates [3]. In order to avoid any interference from coadsorbed species, an oxidation treatment was carried out that would leave a clean V_2O_5 surface, before adsorbing NH_3 and/or NO . The AES spectrum of the vanadia sample after oxidizing it in 40 Torr of oxygen at 675K for 15 minutes followed by heating at the same temperature for 20 minutes in the UHV chamber shows a clean V_2O_5 sample characterized by the presence of the $\text{V}(\text{L}_3\text{M}_{23}\text{M}_{23})$ and $\text{V}(\text{L}_3\text{M}_{23}\text{M}_{45})$ transitions at 430 and 469 eV, respectively, and at 510 eV for the $\text{O}(\text{KLL})$ transition.

Both the adsorption of NH_3 and NO has been carried out as a function of the temperature. The AES spectrum of the V_2O_5 after adsorption of 25 Torr of NH_3 at room temperature (R.T.) shows the presence of a new peak at 377 eV; this peak can be assigned to the $\text{N}(\text{KLL})$ transition indicating that NH_3 can be adsorbed at R.T. After heating the sample to 775K the nitrogen peak disappears. The V_2O_5 should be now reduced. This conclusion is also in agreement with the results of Haber et al. [3] for $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts. On this presumable reduced surface the adsorption of NH_3 is also possible, although no conclusions can be drawn about the nature of the ammonia species on the basis of the AES spectrum.

Evidence for the reduction of the V_2O_5 surface is obtained from TDS experiments. For the oxidized sample two peaks centered at 455 and 485K are evident whereas for the reduced sample only the peak at 455K is present. Taking into account that our mass spectrometer is not

collimated and is physically far away from the sample, the ascription of this first peak remains uncertain. The latter peak can be ascribed to the adsorption of NH_3 through hydrogen bonding to the surface oxygen. If after the ammonia TDS the surface is reduced, we may have eliminated oxygen sites for the formation of the hydrogen bonding between the NH_3 molecule and the surface leading to the disappearance of the TDS peak at 485K.

One of the proposed mechanisms for the $\text{NH}_3 + \text{NO}$ reaction is the so called redox mechanism, which implies the oxidation of NH_3 to N_2O . To test the possibility of such a mechanism several experiments were performed in which instead of analyzing the signal corresponding to A.M.U.15, A.M.U.44(N_2O^+) and 30(NO^+) were analyzed. In both cases a TDS peak at 648K was obtained indicating that V_2O_5 is reduced by NH_3 which in turn is oxidized to N_2O (Figure 32).

Unfortunately the oxidation state of the vanadium species is not unequivocally obtainable by AES. Even at low peak-to-peak modulation (2eV), the intensity ratio between the O(KLL) and $\text{V}(\text{L}_{3\text{M}_{23}\text{M}_{23}})$ lines is the same (2.4). Considering the cross sections for oxygen and vanadium [4], this value represents an oxygen to vanadium atomic ratio of 2.5:1. Although Salzkowski and Somorjai [5] drew some conclusions from the relative intensity of these lines, they were using oxidized vanadium film which means that only with a very thin film of oxide is it possible to get information from this ratio. Another approach to get information about the oxidation state of the 3d transition metal has been depicted by Rao et al. [6,7]. They state that changes on the oxidation state of the transition metal alters the population of the valence band and that is reflected in the relative intensity of the $\text{L}_{3\text{M}_{23}\text{M}_{23}}$ and $\text{L}_{3\text{M}_{23}\text{M}_{45}}$ lines in the Auger spectrum. Since the $\text{L}_{3\text{M}_{23}\text{M}_{45}}$ line implies the 3d level, the change in the 3d valence band population must be reflected in the relative intensity of the above mentioned lines. Again this study, confirmed in this laboratory for vanadium by Lewis et al. [2] has been carried out on thin

25 torr of NH_3 at R.T. on V_2O_5

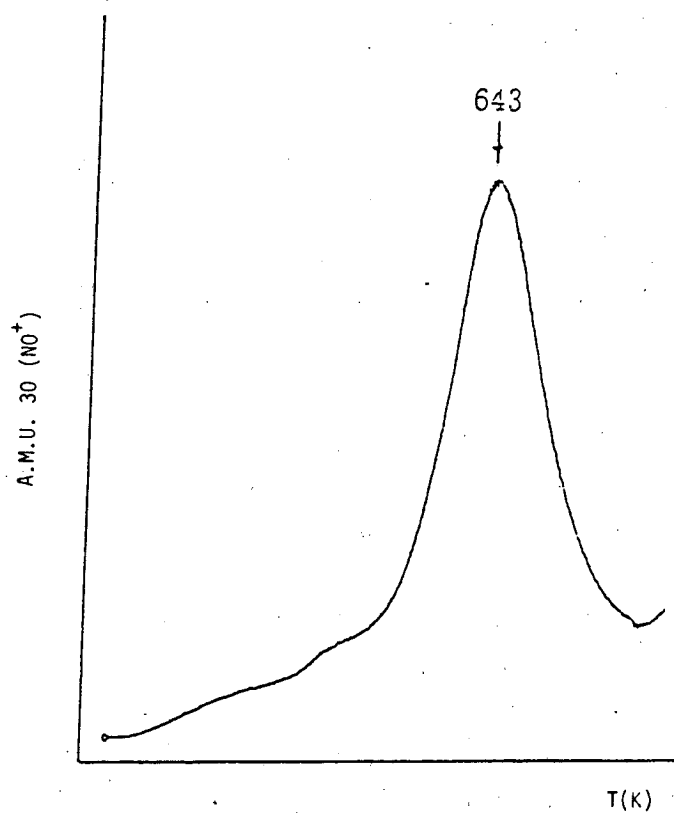


Fig. 32. Thermal Desorption Spectrum of oxidation of NH_3 to N_2O .

oxide films. In our case the relative intensity of the vanadium lines is always equal to 0.95. If we consider that the mean free path for the electrons having kinetic energies around 450 eV is ca. 10 Å, we would have to reduce much of the V_2O_5 structure to notice a substantial change in the AES spectrum. As this is not the general case in catalysis when dealing with powdered catalysts, where only a small amount of the surface sites undergo changes, statements about a surface oxidation state on the basis of AES are not meaningful.

The adsorption of NH_3 has also been studied at 575 and 675K. Essentially, the behavior of the V_2O_5 sample is the same in both cases. A nitrogen peak appears in the AES spectrum that cannot be eliminated by heating at the reaction temperature in vacuum; only by heating at 775K in vacuum does the nitrogen peak disappear.

A TDS profile for the desorption of NH_3 from the V_2O_5 sample previously heated to 675K in 25 Torr of NH_3 was obtained (Figure 33). One peak at 482K is obtained, giving the same desorption energy as the one obtained after ammonia adsorption at R.T. Since after the heat treatment in ammonia the sample was cooled down in an NH_3 atmosphere, this peak may correspond to the adsorption of NH_3 at R.T. However, after heating in vacuum at 675K for 10 minutes the nitrogen peak remains in the AES spectrum. If we now run a new TDS spectrum up to 775K, a new NH_3 (A.M.U. 15) peak appears at 760K which we ascribe to the recombination of NH_2 and H species previously dissociated on the surface at lower temperatures. This ascription finds support in the XPS spectrum for the ammonia adsorption on V_2O_5/TiO_2 catalysts previously reported [8].

While the adsorption of NO was not achieved on a clean oxidized V_2O_5 surface, over the whole range of temperatures studied, NO adsorption at R.T. was observed on a V_2O_5 sample previously reduced with ammonia at R.T. and outgassed at 775K. Heating the sample, after NO adsorption, to 775K the adsorbed species disappears. This result indicates that NO can interact with the reduced vanadium sites. The TDS

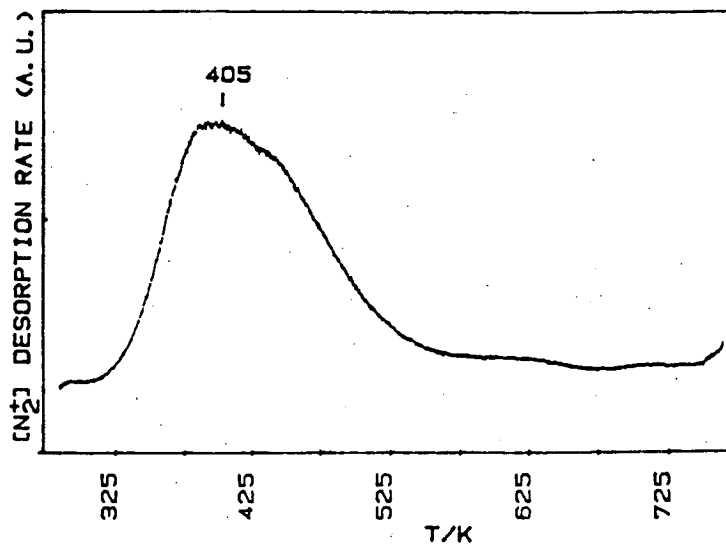


Fig. 33. Adsorption of NO on V₂O₅ on which NH₃ has been preadsorbed.

following A.M.U. $28(\text{N}_2^+)$, shows a peak centered at 435K is observed which indicates that at reaction temperatures the NO can reoxidize the reduced vanadium sites while at the same time being reduced to N_2 .

The adsorption of NO on pure TiO_2 has been studied as a function of both pressure (5×10^{-8} to 25 Torr) and temperature (298 to 725K). Over the whole range of experimental conditions studied, the adsorption of NO takes place on a freshly oxidized titania sample. The spectrum is characterized by a single maximum peaking at 405K slightly asymmetric on the high temperature side when the adsorption takes place at low pressures (ca. 10^{-7} Torr); if the adsorption experiment is conducted at higher pressures (ca. 25 Torr), the shape of the peak remains constant, but the maximum rate of desorption occurs at slightly higher temperatures, 495K, probably due to adsorbate-adsorbate interactions rather than to the interaction with the surface. The spectra obtained are independent of the adsorption temperature within the range studied (298-725K), although the area under the peak is smaller when the adsorption is carried out at the highest temperature.

If after carrying out the TDS experiment a new one is done at the same experimental conditions, a new spectrum that closely resembles the previous one is obtained. Only a decrease in the area under the TDS peak and a shift in the peak position that after several treatments peaks at 395K are noticed.

If instead of selecting the mass-to-charge ratio corresponding to nitric oxide, experiments are performed looking for the evolution of N_2 or N_2O no peaks are obtained.

In order to check if the support, titania (paste), is able to reduce the NO either to N_2 or N_2O , TPRS (Temperature Programmed Reaction Spectroscopy) experiments were carried out. Once the TiO_2 was placed in the sample holder an atmosphere of NO was introduced into the UHV chamber, through a leak valve; the pressure rose to 5×10^{-6} Torr; the

sample holder was then resistively heated and the evolution of both nitrogen ($m/e=28$) and nitrous oxide ($m/e=30$ and $m/e=44$) was monitored by mass spectrometry as a function of the temperature. In these experiments neither nitrogen nor nitrous oxide was detected. The same was true when both NO and NH_3 were contacted on TiO_2 .

From the above results two main conclusions can be drawn: titanium dioxide cannot reduce nitric oxide to N_2 or N_2O and the adsorption of NO poisons the titania surface preventing the readsorption of NO in an open system. This latter conclusion supports the XPS results previously obtained in which a nitrogen peak remains on the surface after heating.

References to XPS, Auger and TDS Studies

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ESR Studies

Various catalysts and their treatment in different gases were studied and are described in the following. The data obtained largely confirm the findings by other techniques which have been described earlier in this report.

Influence of the Phosphoric Acid Content

The effect of the thermal treatment in vacuum and in presence of hydrogen, in the range from room temperature to 500C, has been studied by ESR on three samples with variable phosphorous content (E215 without phosphorous, E283 and E218 with increasing phosphorous content); in an attempt to elucidate the effect of the H_3PO_4 treatment during the sample preparation. Only the results concerning to the H_2 treatments will be analyzed in the following since the comparison with the thermogravimetric measurements is easier.

Samples without treatment showed ESR spectra made by V^{4+} signals, mostly as vanadyl ions. This points to the existence of this ions in the bulk of the vanadium oxide crystallites, since if they were on the surface, they should be oxidized due to the previous calcination in air of the solid or the signal would be wider as a result of the magnetic interaction with oxygen. The signal lineshape is quite different as a result of the phosphoric acid treatment. The main difference is the presence of a broad signal, without resolved hyperfine structure, characteristic of the sample without phosphorus. Moreover, the parameters of the signal with resolved hyperfine structure, corresponding to the E215 sample, are fairly different from those that show the several overlapped signals in the spectra of the phosphorous treated samples. The broad signal, figure 1, for the E215 sample points to the presence of a considerable amount of V^{4+} ions in close vicinity giving rise to strong dipolar interactions that cause the signal to broaden. For the other two samples the resolution of the hyperfine structure indicates that the

vanadyl ions have no interaction among them. The signal parameters for the isolated VO_2^+ species, in the E215 samples, show these ions surroundings are different from the ones for the H_3PO_4 treated samples; probably the vanadyl ions are situated in a different crystallographic phase. In the samples that contain phosphorous, the signal parameters for the vanadyl ions (at least of three different types) are similar for both samples. These different signals could be associated in three different crystallographic phases although the relative proportion of them is different for both samples (E283 and E218).

These results clearly show that the use of H_3PO_4 during the sample preparation favors the dispersion of the vanadium ions, probably through the formation of different vanadium phosphate phases or even titanium phosphate. In these phases that are sometimes observed by XRD, a considerable proportion of the vanadium species may not be at the surface, being unreactive in the reaction. The fact that the active phase may be these crystals, brings some doubts to the previous considerations in the sense that the origin of the support (TiO_2) may be important, at least that it favors one of the different phosphate phases or that the phosphorous decreases the vanadium activity since it covers a portion of the vanadium ions making it difficult to calculate the activity of the surface ions.

H_2 reduction treatments showed, in the case of the E215 sample that on heating to 400°C , a drastic decrease in the signal corresponding to V^{4+} occurs, particularly in the signal corresponding to the less isolated ions, which are the most important in this sample. This effect due to a modification of the V^{4+} ions by reduction or coupling to form a diamagnetic species does not take place as dramatically in the samples that contain phosphorous up to higher temperatures (500°C). The elimination of the V^{4+} signal from the bulk of the sample indicates that the whole crystalline phase, that corresponds to the signal, is being reduced. So that, the fact that in the samples that contain phosphorous the reduction took place at higher temperatures

indicates that the stability of the phosphates is greater against the reduction treatments.

By comparing the spectra of the reduced samples, it can be stated that in the E215 sample (without phosphorous) the only reduced species is vanadium while in turn the presence of both vanadium (V4+) and titanium (Ti3+) is evident in phosphorous containing samples. The presence of reduced titanium ions in the samples that contain phosphorous could indicate that the formation of vanadium phosphates let the TiO_2 be partly exposed and then by H_2 reduction Ti3+ can be obtained. In the absence of phosphorus the disperse vanadium ions are preferentially reduced while the reduction of the titanium species is more difficult.

Influence of the Calcination Temperature

By ESR the effect of the temperature of calcination has been studied on three samples that underwent different thermal treatments during the preparation process. Samples calcined in air at 600C (E285), 700C (E287) and 800C (E312) have been studied. As in the previous section, only the results dealing with the reduction treatments in the presence of H_2 are discussed.

The ESR spectra of the samples calcined in air without further treatments showed signals corresponding to V4+ species in the bulk of the crystalline phases formed. The three samples thermally treated at lower temperatures showed similar lineshape that essentially corresponds to vanadyl species. For the sample calcined at the highest temperature studied, a broad signal appears as the main component of the spectrum. This feature is again interpreted as due to V(IV) species interacting among them causing a broadening of the signal and the disappearing of the hyperfine structure. This behavior is favored in vanadium oxide samples. The fact that practically the signals ascribable to vanadium phosphate disappear when heating at 800C can be interpreted as thermal instability of the vanadium phosphate that evolves to vanadium oxide.

The phosphorus species is probably bonded to the TiO_2 which whether by forming a different phase or by covering by phosphate cannot be reduced to Ti^{3+} by heating in H_2 at 500C.

Treatments in Flow of Different Gases

As a continuation of the previous study on the sample 95-5-0 (without phosphorus), the effect of gas flow treatments has been studied on the E287 sample (calcined at 700C) which is the one that shows the highest activity. By contrast with the study shown above in which the same underwent successive treatments, in this case several portions of the same sample were treated in ammonia and further treated in a gas flow.

The first sample was treated at 250C in a N_2 stream and further ammonia treatment in order to determine whether the reduction of the sample is attainable in an inert gas flow or the reducing characteristics of the ammonia show any influence. The different spectrum ($\text{NH}_3\text{-N}_2$) indicates that the ammonia causes an increase in the broad line without hyperfine structure ascribed to associated V^{4+} ions, in addition, a new signal with hyperfine structure appears. This new line that points to the formation of a new type of V^{4+} ion (as vanadyl ion) is due to a modification of its coordination sphere. After the NH_3 treatment the sample was heated to 250C and NO was flown through the sample. The different spectrum ($\text{NH}_3\text{-NO}$) shows a drastic decrease of the broad line and less intensity for the component due to a certain type of vanadyl ion. This indicates that the sample has been partially oxidized after the NO treatment. Moreover, in the difference spectrum a small axial signal with g perpendicular equal to 2.03 can be observed after the NO treatment. This signal is probably due to the presence of nitroxyl ions.

A new sample was again treated in NH_3 at 250C and further in a mixture $\text{NO} + \text{NO}_2$ (NO_x) at the same temperature. The different spectrum ($\text{NH}_3\text{-NO}_x$) shows an important decrease of the broad signal as well as the resolved structure, once again the sample has been oxidized.

The signal with g perpendicular equal to 2.03 is also present in this case.

The reoxidation of the sample after treatment with NO and NO_x (of greater importance in the latter case) was also observed in the sample 95-5-0.

Treatment with ammonia at 350C gives rise to a spectrum relatively similar to the one obtained after heating in NH_3 at 250C, while in turn the same treatment for the sample 95-5-0 led to a significant decrease in the intensity. This result agrees with the one obtained in the reduction studies that show the intensity of the V^{4+} signal strongly decreases above 300C; however, the sample E287 showed this behavior at temperatures above 400C. After the ammonia treatment, the sample was treated in NO at 350C. The different spectrum (NH_3 -NO) showed the loss of the broad line and the resolved one indicating that the sample was reduced. In the ESR spectrum a narrow line with $g=g_e$ is observed, probably due to electrons trapped in oxygen vacancies. This line also decreases by introducing NO, which again indicates that the sample is oxidized in the presence of NO.

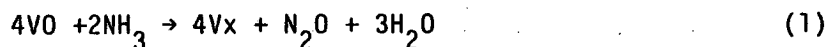
Finally, the sample was treated in NH_3 at 350C and further treated in NO_x at the same temperature. The different spectrum (NH_3 - NO_x) shows a small decrease in the broad signal but the resolved line appears inverted, indicating an increase in its intensity. This seems to indicate that the absence of the broad line is due to a decrease in the V^{4+} interactions as a result of a redistribution of the vanadium ions in the solid or by the appearance of new ligands. The line with $g=g_e$ increases in intensity, again showing that the mixture NO_x has not oxidized the sample. This small effect for NO_x at 350C was also observed in the sample 95-5-0.

MECHANISTIC CONSIDERATIONS

Although the $\text{NH}_3 + \text{NO}$ reaction has been the object of numerous investigations [1], the nature of the active sites and the reaction mechanism are still speculative.

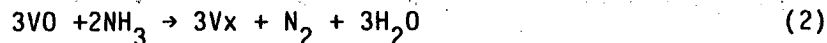
The reduction of V_2O_5 in the presence of NH_3 when supported on TiO_2 has been discussed in the literature [2]. However, a detailed picture of the mechanism of this reaction can still be considered controversial.

Our results with XPS, Auger, and TDS indicate that the surface of the V_2O_5 catalysts is reduced in the presence of NH_3 leaving behind a surface vacancy according to the following scheme:



where VO represents a vanadyl group pointing outwards on the surface of the V_2O_5 catalyst, and Vx represents a surface vacancy, in other words a V^{4+} species.

The reduction of the V_2O_5 surface and the subsequent oxidation of the NH_3 molecule to N_2O has been demonstrated by TDS, Figure 32. This result seems to discard the formation of an $\text{NH}_3\text{-NO}$ adduct as postulated by Miyamoto et al. [3,4]. On the other hand, this result agrees with the scheme proposed by Bosch et al.



In this case, according to Bosch et al. [5], Vx may be a surface vacancy or a surface hydroxyl group; in any case this scheme implies the presence of a surface V^{4+} species as in our scheme.

Although, from our results, it is not possible to discard the presence of hydroxyl groups instead of a surface vacancy, the presence of a surface vacancy is more likely than the hydroxyl group on the basis of our previous results with V_2O_5/TiO_2 catalysts and is also in agreement with the results obtained for the water adsorption on V_2O_5 supported on various oxides [5,6], which show that after H_2O treatment surface vacancies are generated on the surface of the vanadium oxide species at the temperatures used in this study (575-675 K).

Another difference between the stoichiometric scheme proposed by Bosch et al. [5] and the one we propose is the presence of N_2O instead of N_2 . Thermodynamically the N_2O species is stable with respect to its decomposition to N_2 and O_2 at the reaction temperatures (575-675 K), increasing in stability as the temperature increases. Thus, the presence of N_2 instead of N_2O in the reaction products, as postulated, must be due to a further interaction of N_2O with the surface vacancies V_x :



In this way the surface V^{4+} species are reoxidized to V^{5+} while the N_2O is in turn reduced to N_2 . In fact combining eq. (1) and (3) the scheme proposed by Bosch et al. eq. (2), is obtained. Further support for the reduction of N_2O to N_2 is obtained from literature data; in effect, using nitrogen-15 tracer techniques this reduction has been observed on V_2O_4 [4].

We have found that NO species cannot adsorb on V_2O_5 on which ammonia has been preadsorbed, Figure 33. Therefore the activated complex proposed by Miyamoto et al. [3,4] seems to be unlikely. Even when considering the mass spectrometric evidence for the formation of NH_2NO in the NH_3 -NO reaction on vanadium oxide catalysts [7], this path was should be discarded as the main reaction path on V_2O_5 on the basis of our results.

The desorption of N_2O at reaction temperature leaving behind a reduced site makes evident the question of which species is able to reoxidize such vanadium sites. Assuming that the adsorption of NO on the reduced vanadium sites is possible, resulting in their being reduced to N_2 at reaction temperatures, the following elementary step can also be proposed:



By combining eq. (1), (3), and (4) the overall reaction can be described:

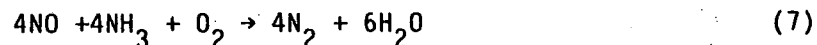


This stoichiometry, proposed by Nam et al. [7] for the NH_3+NO reaction on V_2O_5/TiO_2 catalysts, cannot explain the drop in NO conversion in the absence of O_2 reported in the literature [6] and in results on our V_2O_5/TiO_2 catalysts.

Taking into account the presence of O_2 in the reaction mixture, the following step can also be postulated:



the overall reaction may then be written as:



which is in good agreement with previous results [2] and with the stoichiometries proposed by Mizumoto et al. [8].

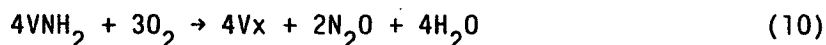
However, the elementary steps described above cannot explain the presence of ammonia adsorbed on the vanadium catalyst at reaction temperatures; in addition this catalyst is unreactive towards NO. A

strongly adsorbed species might be understood as NH_3 molecules that dissociate on the surface of the reduced V_2O_5 sample according to the following:



This VNH_2 species finds support in the XPS data previously reported and in literature data [8]. Thus, Otto et al. [9,10] claim that the primary step in the $\text{NH}_3 + \text{NO}$ reaction is the formation of NH_2 species. Additionally, spectroscopic evidence for the formation of NH_x species has been also extensively reported [10, 11].

O_2 treatment at 675 K restores the original V_2O_5 surface lending support to the oxidation of such VNH_2 species in the presence of oxygen. The stoichiometric step should be described by:



By combining the elementary steps described by eq. (5 to 10), the side reaction that leads to the increase in N_2O concentration as the reaction temperature increases is obtained:



This side reaction may explain the maximum on the NO conversion vs. temperature curves. If a competitive adsorption between NO and NH_3 for the reduced vanadium sites takes place, the number of sites available for the reduction of NO might decrease leading to a drop in NO conversion; in addition, in the presence of O_2 , the VNH_2 species are oxidized to V^{5+} and N_2O , increasing the N_2O concentration in the reaction products.

However for the case of supported V_2O_5 other pathways for the

production of N_2O may be considered, particularly the fact that TiO_2 is able to produce N_2O [6]. In the case of TiO_2 there are two possibilities: the oxidation of strongly held ammonia species by the TiO_2 surface which could also be responsible for the production of N_2O ; or the interaction of two NO molecules on the TiO_2 surface. The latter assumption may be supported by the presence of a N(1s) band in the XPS spectra of V_2O_5/TiO_2 catalysts after reacting them with 25 torr of NO at 675 K [2].

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CONCLUSIONS

The adsorption of NH_3 and NO on pure and supported vanadia catalysts at pressures (up to 25 torr) and temperatures (R.T. to 875 K), near industrial ones, has been studied by XPS, AES, and TDS, using an UHV chamber equipped with a built-in high pressure cell (up to 1 atm.).

NH_3 adsorption takes place over the whole range of temperatures studied on both V_2O_5 as well as reduced V_2O_5 surfaces while NO adsorption occurs only on reduced surfaces. Differences between pure and supported V_2O_5 are not evident, while NO adsorption on oxidized $\text{V}_2\text{O}_5/\text{TiO}_2$ surfaces, in the temperature range studied, should be a determinant factor in the catalyst efficiency.

The $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst currently employed for reducing NO_x emission from power plants can be understood as a bifunctional catalyst. In effect, the adsorption of ammonia takes place mainly on the vanadium component causing the reduction of the original V^{5+} species to V^{4+} ones. In turn the NO adsorption takes place on the TiO_2 support since oxidized vanadia samples are completely unable to adsorb NO. The reduction of NO to N_2 would occur through a Langmuir-Hinshelwood mechanism or a spill-over on the surface of the vanadia component that implies the migration of the adsorbed NO species from the support to the reduced vanadium species. In the absence of O_2 , however, the catalyst loses activity since the reduced vanadium species interact with ammonia molecules in the gas phase leading to the formation of V-NH_x species completely unreactive towards NO species.

Some clues have also been obtained on the influence of the extrusion lubricant, phosphoric acid, on the activity of the extruded

catalysts. XPS measurements have shown that once extruded the surface is phosphate enriched while in turn the amount of vanadium species at the surface is drastically decreased with respect to the non-extruded catalysts. This may propose the formation of vanadyl phosphate in which the PO_4^{3-} groups are pointing outward the surface. As a result of this the catalytic activity for the reduction of NO species is lowered.

Furthermore, oxidation of the NH_3 species to N_2O has been demonstrated by TDS on oxidized vanadium species that are partially recovered by subsequent reduction of the N_2O species to N_2 . Since TiO_2 was not able by heating in NO at reaction temperatures to generate N_2O , a similar redox cycle on the surface of the support involving ammonia is proposed. This also leads to the formation of NH_x species on the surface of the catalyst that, in the presence of O_2 , leads to the formation of N_2O as has been reported in the literature. This process also explains the decrease in the catalytic activity as a function of the temperature as a result of the poisoning of active surface sites.

II. REPORT CONCLUSIONS

A careful investigation with many tools has been undertaken of the reaction of NO_x and ammonia over vanadia-titania catalysts in the presence of oxygen. An understanding of a novel mechanism has been achieved which indicates that the catalytic reaction is essentially a redox reaction of 5 valent and 4 valent vanadia. In an attempt to produce improved catalysts, it has been proposed to use pelleted catalysts instead of the honeycomb catalysts currently being used commercially. This would save a great deal of expense in catalyst manufacture, but requires that the pelleted catalysts be hard enough to withstand abrasion at very high gaseous space velocities. It has been found that extrusion of titania containing vanadia in the presence of some phosphoric acid as a binder gives sufficiently hard catalysts which, however, show a loss of activity of about 10%. This loss of activity has been traced to the formation of surface vanadium phosphates and titanium phosphates. Life tests have shown that while this loss of activity prevails over long periods of time, the activity curve for the non-phosphorous containing and the phosphorous containing catalysts are parallel. It has also been shown that by reducing the space velocity by about a factor of 2, activities of the phosphorous containing catalysts match that of the non-phosphorous containing catalysts. This means that the catalyst volume will have to be about double, which probably still presents an advantage over the expensive honeycomb catalyst.

A mechanism for the reaction of NO and NH_3 on $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts has been proposed which involves a redox reaction. V_2O_5 is reduced by ammonia and the lower valent vanadium species is reoxidized by NO. Oxygen is required to inhibit the formation of a V-NH₂ species. Since V_2O_5 does not sorb NO and TiO_2 does, a spill-over of NO to the reduced vanadia surface is hypothesized.

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